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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

1338. **The dawn of micro-analysis.** C. Duval (Micro-anal. Res. Lab., 11 rue Pierre Curie, Paris, France). *Mikrochim. Acta*, 1960, (5-6), 630-635 (in French).—A historical review of 18th and 19th century micro-analytical researches, with 36 references. J. P. STERN

1339. **The origins of colorimetric analysis.** F. Szabadváry (Inst. Gen. Chem., Tech. Univ., Budapest, Hungary). *Talanta*, 1960, **5** (2), 108-111 (in German).—The development of colorimetric analysis during the period 1845 to 1880 is outlined, and a list of authors of the period and 19 references are given. W. T. CARTER

1340. **Progress in microchemistry.** *Microchem. J.*, 1960, **4** (3), 271-396.—The following review papers are included. **Progress in reduced-scale determination of physical constants: 1959,** J. S. Wiberley and H. W. Drake, 277-287 (57 ref.). **Progress in fractionation procedures. Differential migration methods: 1959,** A. G. Mistretta, 289-305 (112 ref.). **Progress in quantitative inorganic analysis: 1959,** R. Maurmeyer, 307-320 (58 ref.). **Progress in biochemical investigations. I. Nitrogen compounds: 1959,** S. Natelson, 321-342 (202 ref.); **II. Determination of elements in biological systems: 1959,** A. L. Levy, 343-352 (81 ref.). **Progress in elemental quantitative analysis: 1959,** A. Steyermark and B. E. McGee, 353-372 (165 ref.). **Progress in organic functional group analysis: 1959,** T. S. Ma, 373-386 (57 ref.). **Progress in equipment and tools: 1959,** H. J. Francis, jun., 387-396 (104 ref.).

1341. **Determination of gases in metals.** Report of a Symposium organised by The Society for Analytical Chemistry, The Iron and Steel Institute and The Institute of Metals. *Iron and Steel Inst., Spec. Report* No. 68, 1960; 308 pp.—The following papers are included. **Sampling of liquid metals,** T. B. King, pp. 3-18. **The determination of oxygen in metals: a review,** W. T. Elwell, pp. 19-42. **The determination of gases in metals by vacuum fusion,** J. E. Still, pp. 43-63. **The determination of gases in metals by the semi-micro vacuum-fusion technique,** A. Parker, pp. 64-74. **An assessment of carrier-gas methods for the determination of gases in metals, with particular reference to steel,** C. E. A. Shanahan, pp. 75-92. **The determination of oxygen in beryllium by activation analysis,** R. F. Coleman, pp. 93-102. **Emission spectrometric determination of oxygen, nitrogen and hydrogen in metals,** V. A. Fassel, pp. 103-120. **The determination of oxygen and nitrogen in iron and steel by an isotope-dilution method,** M. L. Pearce and C. R. Masson, pp. 121-132. **The determination of nitrogen in metals: a review,** J. D. Hobson, pp. 151-182. **The determination of nitrides in metals,** H. F. Beeghly, pp. 183-191. **The determination of hydrogen in metals,** R. E. Eborall, pp. 192-218. **The determination of hydrogen in cast iron,** J. V. Dawson and L. W. L. Smith, pp. 219-228. **An improved carrier-gas technique for the determination of hydrogen in steel,** F. R. Coe and N. Jenkins, pp. 229-235. **X-ray emission analysis and the determination of gases in metals,** T. Mulvey, pp. 255-269. **Application of internal-friction measurements to the study of gases in metals,** G. M. Leak, pp. 270-295.

1342. **Use of nuclear magnetic resonance for analytical purposes.** N. M. Pomerantsev. *Zavod. Lab.*, 1960, **26** (8), 950-956.—A review, with 29 references, is presented. G. S. SMITH

1343. **Notes on the behaviour of diphenylcarbazone as an analytical reagent.** J. Minczewski and W. Żmijewska (Inst. Nucl. Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (3), 429-433.—During the investigation of the Cr^{6+} - diphenylcarbazide (**I**) reaction it was found that diphenylcarbazone (**II**) in alcoholic soln. deteriorates on storage. The decomposition of 0·01M-**II** proceeded at a steady rate until about 75% of **II** was destroyed after 35 days, and after 3 months virtually no **II** remained in the soln. It was also confirmed that **II** in glacial acetic, formic and propionic acids produced nearly the same colour as that produced in the Cr^{6+} - **I** reaction, which would suggest that the colour is not due to a complex, but to a tautomeric form of **II**. P. BRYCH

1344. **The thermal properties of some amine tetraphenylboron salts. 8-Hydroxyquinoline and its derivatives.** W. W. Wendlandt, J. H. van Tassel and G. R. Horton (Dept. of Chem., Texas Technol. Coll., Lubbock, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 332-336 (in English).—Confirmation has been made of the existence of compounds having the composition A_2B, where B is the tetraphenylborate ion and A is 8-hydroxyquinoline, 8-hydroxy-2-methylquinoline, 5,7-dichloro-8-hydroxyquinoline, 5,7-dibromo-8-hydroxyquinoline or 8-hydroxy-5,7-di-iodoquinoline. The stability of the salts has been studied by thermogravimetric and by differential thermal analysis. The 5,7-dihalo-compounds show greatest stability. T. R. ANDREW

1345. **Complexans. IV. Synthesis and study of complexans of the triazine series.** R. P. Lastovskiĭ, I. D. Kolpakova and N. M. Dyatlova (All-Union Sci. Res. Inst. for Chem. Reagents, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 419-423.—4,6-Diamino-2-hydroxy-1,3,5-triazine-*NNN'N'*-tetra-acetic acid (**I**) and 2,4,6-triamino-1,3,5-triazine-*NNN'N'N"N"*-hexa-acetic acid (**II**) were synthesised. **I** forms compounds at pH 2·5 with Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Ni^{2+}, Mo^{6+} and Ti^{4+}, and also with

As^{3+} and Mn^{2+} at pH 4·4; at pH 9·35 it forms compounds with Pb^{2+}, Cu^{2+}, Cd^{2+}, As^{3+}, Co^{2+} and Mo^{6+}; and at pH 12 with Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Bi^{3+}; **II** forms compounds at pH 4·4 with Pb^{2+}, Cu^{2+}, Mn^{2+}, Mo^{6+} and Ti^{4+}, and also with La^{3+}, Tl^{+} and Zn^{2+} at pH 2·5; at pH 9·3 it forms compounds with Pb^{2+}, Cu^{2+}, As^{3+}, Mn^{2+}, Mo^{6+} and La^{3+}; and at pH 12 with Cu^{2+}, Cd^{2+}, Ni^{2+} and Mo^{6+}. For this study, differential polarography was used. The properties of **I** and **II** are compared with those of *m*-phenylenediaminetetra-acetic acid. K. R. COOK

1346. **New mixed indicator for mercurimetry.** R. D. Glukhovskaya and N. A. Ugol'nikov. *Izv. Vÿssh. Ucheb. Zavedeniĭ, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 49–51; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 72,967.—The mixed indicator containing diphenylcarbazone (**I**) and 2-nitroso-1-naphthol (**II**) is used for the mercurimetric titration of halides. Both components are mercurimetric indicators, and also show oxidation - reduction properties (in alkaline soln. **I** and **II** are orange; in acid soln. **I** is colourless and **II** is yellow - green). The mixed indicator can thus be used to establish the required pH of the soln. at the beginning of the titration; if acid or neutral halide soln. are neutralised with alkali to an orange colour, and N-HNO_3 is added to a yellow - green colour, a suitable pH for the titration is obtained. At the end-point, the violet colour of the complex of Hg^{2+} with **I** and the orange colour of the complex of Hg^{2+} with **II** are superimposed, giving a cherry-red soln.; the colour change from yellow - green to cherry red is sharp and is easily seen, even with fairly dilute soln. (0·01N). The clearest colour change is obtained with 1 drop of 1% ethanolic **I** soln. and 1 drop of 3% ethanolic **II** soln. for each 5 or 6 ml of soln. A mixed indicator containing **I** and **II** in the same proportions gives similar results. The colour change is made sharper by titrating Cl^-, Br^- and I^- in an aq. ethanolic medium. C. D. KOPKIN

1347. **Nitrophenylosazones and nitrophenylhydrazones as indicators for high pH values.** N. V. Chugreeva (Saratov Univ., USSR). *Zhur. Anal. Khim.*, 1960, **15** (4), 391–393.—The indicator properties of the 2, 4-dinitrophenylhydrazones of dihydroxytartaric acid, pyruvic acid and acetone, and of the *p*-nitrophenylosazone of dihydroxytartaric acid, were studied. It is shown that, in the temp. range 0° to 80°, these compounds can be used in soln. containing a high concn. of salts, ethanol or gelatin. Indicators of the hydrazone series can also be used for the photometric measurement of pH in the range 11·5 to 13·5, with an error of 0·1 to 0·2 per pH unit; Ca^{2+}, Sr^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ag^{+} and Cd^{2+} can be present up to molar concn.; Mg^{2+} and Ni^{2+} interfere. K. R. COOK

1348. **Characterisation of the colour quality of indicator transition. Complementary tristimulus colorimetry.** C. N. Reilley, H. A. Flaschka, S. Laurent and B. Laurent (Dept. Chem., Univ. of North Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1218–1232.—The over-all quality of an indicator end-point is a composite function of the sharpness and colour quality of the transition. The former is related to the rate of reaction and the equilibrium constants and can be calculated rigorously, while the latter involves the colour phenomena in the soln. and their relation to the observing eye. By combining the principles of tristimulus colorimetry with Beer's law, formulae are developed to permit the complete characterisation of the colour quality factor, including a mathematical treatment of screening, dichromatism and the need for colour memory in many transitions. The theory permits the calculation of the relative quantities of inert dyes needed for screening an indicator; Kiton yellow 7GF (C.I. Acid Yellow 3), Acid red GA (C.I. Acid Red 1), FD & C Violet No. 1 (C.I. Acid Violet 49) and Brilliant blue FCF (C.I. Acid Blue 9) are particularly suitable for this purpose. A. R. ROGERS

1349. **The thermal stability of analytical standards.** C. Duval and C. Wadier (Lab. de Rech. Microanal., Paris). *Anal. Chim. Acta*, 1960, **23** (3), 257–261 (in French).—Decomposition curves obtained by means of the thermal balance are presented for 12 salts, *viz*, Ba acetate, Pb acetate, $Pb(NO_3)_2$, KNO_3, $MgCl_2$, NH_4NO_3, ammonium citrate, $Co(NO_3)_2$, $UO_2(NO_3)_2$, Na terephthalate, Na_2S and K palmitate. Their i.r. spectra between 6 and 15 μ have been examined, with soft paraffin as a binder and sodium chloride optics. It is concluded that Pb acetate, $MgCl_2$, $Co(NO_3)_2$ and Na_2S cannot be weighed directly for the preparation of standard soln. H. M.

1350. **Qualitative inorganic analysis. XVI. Use of a solution of hydrogen sulphide in acetone for the precipitation of the copper - tin group of metals.** W. I. Stephen (Dept. of Chem., Univ. Birmingham, England). *Mikrochim. Acta*, 1960, (5–6), 927–934 (in English).—A saturated ($\simeq$ 2%) soln. of H_2S in acetone is stable for at least 3 months in the absence of H_2O or acid. For pptn. of the Cu - Sn group, after removal of alkaline-earth metals, a sample vol. of 1·5 ml and an acid concn. of 0·35N are recommended. If As is absent, 5 or 6 drops of reagent are added, the soln. is warmed, and 2 or 3 drops more are added to ensure complete pptn. If As is present, 4 drops of 10% NH_4I soln. are added first. *Preparation of reagent*—Wash H_2S from a Kipp's generator with H_2O, dry with silica gel, and absorb in acetone (previously dried over anhyd. Na_2SO_4) which is chilled in salt and ice. Pass the gas until a saturated soln. is obtained. P. D. PARR-RICHARD

1351. **Ion-exchange separation of groups of elements. III. Elements of the copper group.** B. K. Preobrazhenskiĭ and Yu. P. Saĭkov. *Radiokhimiya*, 1960, **2** (1), 68–72; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,013.—A scheme is proposed for the qual. separation of elements of the copper group (Cu, Hg, Bi, Cd and Pb) by sorption by the cationite KU–2.

IV. Elements of the third analytical group. B. K. Preobrazhenskiĭ, V. P. Tsvelikhovskiĭ and V. I. Mel'nikov. *Ibid.*, 1960, **2** (1), 73–77.—The method is based on the sorption from conc. HCl of the components (Mn, In, Ti, Hf, Zr, Co, Fe, Ga, U and Zn) by Dowex 1 (Cl^- form) and elution with various concn. of HCl. The elements not adsorbed (Cr, Be, V^{IV}, Tl^{I}, Ni, Al and the rare-earth metals) can be adsorbed by the cationite KU–2 (H^+ form) and eluted by various methods. C. D. KOPKIN

1352. **Separation of cations by ion-exchange adsorption.** D. V. Bezuglyĭ, M. P. Borovshchuk and N. E. Khomenko. *Trudÿ Khar'kovsk. Politekh. Inst.*, 1959, **26**, 59–61; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,014.—The method is based on the difference in the stability of the complexes of the cations with EDTA (disodium salt) (**I**), and has

been tested on synthetic mixtures prepared by dissolving freshly precipitated and washed $Fe(OH)_3$ in **I** with subsequent addition of known amounts of $CuSO_4$ and $MnSO_4$ and adjustment of the pH of the soln. to 1·7 to 1·8. The soln. was passed through a column containing 3 g of cationite KU-1 (H^+ form), and the column washed and eluted with 0·5N-HCl (4 × 25 ml). The method provides an efficient separation of micro amounts of Cu and Mn from Fe. It was not possible to remove Cu quant. from Zn with cationite KU-1 or anionite AN-2F, which is attributed to the small difference in the instability constants of the complexes of these cations with **I**. C. D. KOPKIN

1353. **Chemical applications of complementary tristimulus colorimetry.** C. N. Reilley and E. M. Smith (Dept. of Chem., Univ. of North Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1233–1240.—The principles of complementary tristimulus colorimetry have been extended to the quant. analysis of mixtures of two or three comcomponents with overlapping spectra, and the determination of dissociation constants of acids and the formulae and stability constants of complex ions. A simple analogue computer (described) is used to calculate chromaticity co-ordinates within 3 min. from data obtained by the weighted ordinate method at 10 wavelengths. A. R. ROGERS

1354. **Three-dimensional representation of voltammetric processes.** W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1509–1512.—Relationships established by time-dependent voltammetry are represented on a three-dimensional surface. Intersections thereon may represent polarography, chronopotentiometry, polarography at a stationary electrode, and constant-potential voltammetry. Good agreement is obtained with more rigorous theoretical treatments. The technique is applicable to linear-current-scan chronopotentiometry and to spherical electrodes. J. P. STERN

1355. **Chronopotentiometry with current reversal. Application to *p*-benzoquinoneimine hydrolysis.** A. C. Testa and W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1512–1514.—By this technique it is possible to prepare an unstable compound electrochemically and then to follow the course of its decomposition when the current is reversed. The technique is illustrated by the anodic oxidation of *p*-aminophenol to *p*-benzoquinoneimine and subsequent decomposition of the latter compound. The reactions were carried out at constant current in various concn. of H_2SO_4 and with a wide range of times before current reversal. The rate constant of the decomposition could be deduced from the ratio of the time to current reversal and the time to the first decomposition wave. G. BURGER

1356. **Chronopotentiometric potential - time curves and their interpretation.** W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1514–1517.—Expressions are derived for the potential - time relations for 14 reduction mechanisms. Criteria are presented by which these mechanisms can be distinguished. G. BURGER

1357. **Chemical kinetic parameters from chronopotentiometric potential - time measurements.** A. C. Testa and W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1518–1520.—The errors involved in the calculation of rate constants from chronopotentiometric curves are discussed. The rate constant determined by Snead and Remick (*J. Amer. Chem. Soc.*, 1957, **79**, 6121) by potential - time measurement for the reduction of *p*-benzoquinoneimine differs from that determined by the present authors (*Anal. Chem.*, 1960, **32**, 1512) by chronopotentiometry with current reversal. A method of calculation based on the fitting together of two curves, one derived from the error function and the other from the experimental results, is presented. The possible error due to the effect of the electrical double layer and the potential gradient in the soln. is considered and found to be negligible. G. BURGER

See also Abstracts—**1608**, Titration of EDTA and DCyTA. **1663**, Metallochromic indicator for Ca.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

1358. **Flame-photometric methods in metallurgical analysis. A review.** J. A. Dean (Dept. of Chem., Univ. of Tennessee, Knoxville, U.S.A.). *Analyst*, 1960, **85**, 621–629.—The general possibilities of the application of flame photometry to the analysis of metallurgical products are discussed. Methods for determining constituents in various types of ferrous and non-ferrous alloys are reviewed under the heads of the elements to be determined. In many methods, solvent extraction serves to isolate the element in a form suitable for photometric determination. The wavelengths, type of emission, and type of flame useful for the elements considered are tabulated, together with the emission sensitivities in p.p.m. (57 references.) A. O. JONES

1359. **Present state of methods for determining impurities in semi-conductor materials.** I. P. Alimarin and Yu. V. Yakovlev. *Zavod. Lab.*, 1960, **26** (8), 915–921.—A review with 48 references is presented. G. S. SMITH

1360. **The oxidation of some inorganic systems by lead tetra-acetate.** A. Berka, V. Dvořák, I. Němec and J. Zýka (Inst. for Anal. Chem., Charles' Univ., Prague). *Anal. Chim. Acta*, 1960, **23** (4), 380–384 (in French).—Soln. of Pb tetra-acetate free from Pb^{II} may be prepared by dissolving Pb_3O_4 in hot glacial acetic acid, crystallising out Pb tetra-acetate and re-dissolving it in acetic acid. The soln. may be used for the direct potentiometric titration of Cr^{2+}, Ti^{3+}, Fe^{2+}, Sn^{2+}, Sb^{3+} and As^{3+} in acid soln. (HCl or H_2SO_4 up to $\simeq$ 4N). T. R. ANDREW

1361. **Indirect volumetric determination of anions with redox indicators.** Z. Gregorowicz (Inst. anorg. Chem., Schlesische Techn. Hochschule, Gliwice, Poland). *Anal. Chim. Acta*, 1960, **23** (3), 299 (in German).—Sulphate, CrO_4^{2-} and PO_4^{3-} can be determined by reaction with an excess of 0·1N-$Pb(NO_3)_2$ in soln. buffered with acetic acid - Na acetate. The ppt. is filtered off and washed, and the excess of $Pb(NO_3)_2$ is titrated with 0·1N-$K_4Fe(CN)_6$ in the presence of 1 drop of 0·1N-$K_3Fe(CN)_6$ and 3 drops of 1% aq. Variamine blue acetate. The end-point is marked by a change in colour of the soln. from violet to milky yellow. The titration is carried out at $\simeq 60°$. Bi- and ter-valent ions interfere, as do large amounts of Na, K, or ammonium salts. H. M.

1362. **Solvent extraction behaviour of some metal - 1-(2-pyridylazo)-2-naphthol chelates.** Shozo Shibata (Gov. Ind. Res. Inst., Nagoya, Japan). *Anal. Chim. Acta*, 1960, **23** (4), 367–369 (in English).—The extractability and colour of the extract is reported for the 1-(2-pyridylazo)-2-naphthol complexes of Ga, In, Cu, Bi, Ni, Zn, Fe, Hg, Mn, Co, Cd, Pb, Ce, Y and La for CCl_4, benzene, $CHCl_3$, ethyl ether and isoamyl alcohol. The absorption spectra and the effect of pH on extraction are reported for the complexes with Ni, Mn, Ga, In, Cd, Zn, Hg and Fe, together with the peak wavelengths for absorption and the molar extinction coefficients. T. R. Andrew

1363. **Ultra-violet spectra of some inorganic solids.** W. H. Waggoner and M. E. Chambers (Univ. Georgia, Athens, U.S.A.). *Talanta*, 1960, **5** (2), 121–126 (in English).—Ultra-violet spectra are presented for 9 sulphates, 3 chromates and 2 nitrates in aqueous soln. and in the solid state as KBr discs. The results on soln. were inconclusive except for the chromates, which gave maxima at 270 mμ and 370 mμ. With solid samples the sulphates gave maxima at 260 and 300 mμ, the chromates at 275 and 375 mμ and the nitrates at 280 to 290 mμ. The application of the technique to the qual. analysis of solid mixtures is described. W. T. Carter

1364. **Spectrophotometric titration of bivalent metals with 1-nitroso-2-naphthol in dimethylformamide.** I. T. Takahashi and R. J. Robinson (Dept. of Chem., Univ. of Washington, Seattle, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1350–1352.—Small amounts (5 to 10 μmoles) of Cu and Ni may be titrated with a standard soln. of 1-nitroso-2-naphthol in dimethylformamide ($\simeq$ 0·005M) with photometric determination of the end-point. For Ca, best results are obtained at 600 mμ in 0·0015M-acetic acid in dimethylformamide ($\simeq$ 40 ml), while, for Ni, 525 mμ and a soln. containing 5 ml of butylamine and 35 ml of dimethylformamide are used. Results are reproducible to better than 1%. It was not possible to devise satisfactory conditions for the determination of Zn^{II}, Pb^{II} or UO_2^{II}. T. R. Andrew

1365. **Quantitative determination of the constituents of mixtures of non-corrosive light gases by the M.S.3. mass spectrometer.** U.K.A.E.A. (Production Group, Capenhurst). U.K.A.E.A. Report PG164 (CA), 1960. 13 pp.—Full experimental details are given of a procedure that is particularly suitable for the determination of H, He, O, N, Ar, CO and CO_2. The coefficient of variation is estimated to be 5% at the 1% level. G. J. Hunter

1366. **Use of ring-oven spot colorimetry with the aid of a silver sulphide standard scale in inorganic paper chromatography.** M. B. Ćelap and H. Weisz (Chem. Inst., Belgrade, Yugoslavia). *Mikrochim. Acta*, 1960, (5–6), 706–712 (in German).—The technique previously described (Weisz *et al.*, *Ibid.*, 1959, **36**) is applied to the semi-quant. determination of Pb, Cu and Cd, and Fe, Co and Zn, previously separated by paper chromatography, in the range 0·5 to 2 mg per ml with an accuracy within ± 6%. J. P. Stern

1367. **Use of the ring oven in trace analysis.** G. Ackermann (Inst. f. Inorg. Chem., Bergakad. Freiberg, Sachsen, Germany). *Mikrochim. Acta*, 1960, (5–6), 771–774 (in German).—Trace impurities in alkali- and alkaline-earth-metal salts are concentrated by pptn. as hydroxides or sulphides and collected on micro-filters (illustrated). These impurities are then examined by the ring-oven technique. The limit of sensitivity for the detection of Cu^{2+} and Fe^{3+} in 100 ml of N-KCl or N-Ca acetate is 10^{-3} p.p.m. J. P. Stern

1368. **Separation of ions on filter-paper strips in dissolution and precipitation zones.** E. Schwarz-Bergkampf (Chem. Inst., Montanist. Hochsch., Leoben, Austria). *Mikrochim. Acta*, 1960, (5–6), 755–757 (in German).—In this extension of the ring-oven technique to paper strips, the strips are supported in a special device (illustrated) so that they may be warmed over a micro-flame. Soln. of ions can be evaporated, leaving bands that can be further treated chemically, or fractionally dissolved and then pptd. on bands of reagents deposited on the paper; Fe^{III}, Ni and Co (as chlorides) can thus be identified by movement of Ni and Co down the paper through bands of diacetyl dioxime and 1-nitroso-2-naphthol (the coloured ppt. being readily identified), whilst the $Fe(OH)_3$ remains stationary and is identified with $K_4Fe(CN)_6$. Difficulties encountered in the use of this technique include decomposition of the paper under acidic conditions and the slow movement of Cu in ammoniacal soln. J. P. Stern

1369. **Analysis of metal chelates by gas chromatography.** W. J. Biermann and H. Gesser (Dept. of Chem., Univ. of Manitoba, Winnipeg, Canada). *Anal. Chem.*, 1960, **32** (11), 1525–1526.—Metals in the form of acetylacetonato-complexes have been successfully separated on columns (4 ft. × 0·25 in.) of Apiezon L grease on glass beads 200 μ in diameter. The complexes of Al and Be are separated from a soln. in acetylacetone and those of Al and Cr from a soln. in CCl_4. An argon ionisation detector is used. C. B. Baines

1370. **Extractive radiometric titration.** H. Spitzy (Paracelsus Inst., Bad Hall, Upper Austria). *Mikrochim. Acta*, 1960, (5–6), 789–802 (in German). —The method of Duncan and Thomas (*J. Inorg. Nuclear Chem.*, 1957, **4**, 376) is applied to the microgram range. A new measuring head, incorporating a stirrer and automatic discharge seal, is illustrated. The method is applied to the radiometric titration of Ag, Zn, Co, Cu and Hg with dithizone with a non-isotopic or an isotopic indicator. Determinations of 10 μg are possible with high accuracy. J. P. Stern

1371. **X-ray fluorescence method for determination of the transition-metal content in very small specimens of alloys.** P. J. Brown (Crystallographic

Lab., Cavendish Lab., Cambridge, England). *J. Sci. Instrum.*, 1960, **37** (10), 394–397.—The ratio of the intensities of the characteristic X-rays emitted by two fluorescing elements in the specimen is measured, and compared with the same ratio determined for a number of specimens of known composition in the same physical state. When only one fluorescing element is present a known amount of a second must be added. An accuracy better than 1% is possible for specimens containing as little as 0·2 mg of the transition metals.

G. Skirrow

1372. **Spectrographic determination of metals in welding alloys.** E. S. Kudelya. *Avtomat. Svarka*, 1960, (3), 76–79; *Ref. Zhur., Khim.*, 1960, (17), Abstr. No. 69,246.—This is a modification of a method described previously [*Ref. Zhur., Khim.*, 1955, (8), Abstr. No. 14,900]. High concn. of Cr, Ni, Mn and W can be determined with an error of 4%. The comparison elements used are Fe and Ni.

K. R. Cook

1373. **Paper electrophoresis of mineral cations in the presence of complexing agents.** P.-E. Wenger, I. Kapétanidis and W. von Janstein (Univ. de Genève, Switzerland). *Mikrochim. Acta*, 1960, (5–6), 961–966 (in French).—The migration of Ag, Hg^{2+} and Pb in the presence of 1,2-di-(2-aminoethoxy)ethane-*NNN'N'*-tetra-acetic acid at different pH values is discussed and suitable buffer soln. from pH 2 to pH 12 are given. With Ag, considerable tailing occurs at low pH values; at pH > 9, migration is anodic and a good spot is obtained. At pH 2, Hg migrates to the anode and Pb to the cathode, but at pH 3 migration of Pb also becomes anodic. Separation of binary mixtures of these ions should be possible.

P. D. Parr-Richard

1374. **Chelatometric determination of aluminium, nickel and manganese without prior separation.** D. H. Wilkins (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 309–311 (in English).—To the sample soln. add a known vol. (in excess of that required) of hydroxyethylethylenediaminetriacetic acid (HEDTA) (**I**), adjust the pH to 5, add 10 ml of M-Na acetate - M-acetic acid buffer, and boil, then cool the soln. to room temp. and add 3 drops of a 1% soln. of Methyl Calcein or Methyl Calcein Blue [condensation products of sarcosine (*N*-methylglycine) and formaldehyde with fluorescein or with 4-methylumbelliferone, respectively] and back-titrate with standard Cu^{II} soln. to determine Al plus Ni. (The end-point is shown by a quenching of the fluorescence of the indicator.) Add NH_4F (0·5 g), heat to boiling, and titrate the **I** liberated from the aluminium complex with standard Cu^{II} soln. Add 1 g of K tartrate, adjust the pH to 9·5 with NaOH, and titrate Mn^{II} with EDTA. Results on mixtures of $\simeq$ 10 mg of each element show recoveries within $\pm$ 0·1 mg.

T. R. Andrew

1375. **Automatic derivative spectrophotometric titration of excess EDTA in the determination of cobalt, copper or iron.** H. V. Malmstadt and T. P. Hadjiioannou (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (3), 288–293 (in English).—To the sample soln. are added Calcein W (**I**), as indicator, and a slight excess of EDTA (disodium salt) soln., shown by the appearance of a green fluorescence. This excess of EDTA is titrated automatically in the "Spectro-Electro" derivative titrator with standard $Cu(NO_3)_2$ soln., the **I** then functioning as an absorption indicator. An increase in absorbance at 500 mμ occurs when the excess of EDTA and the indicator have reacted completely with the titrant, and this is the signal for the automatic termination of the titration. The sample soln. is buffered to pH 4·4 with Na acetate - acetic acid, 4 drops of indicator soln. (0·1% of **I** in 0·001N-NaOH) are added and 0·04M-EDTA (disodium salt) is run in until a green fluorescence appears. The determination is then finished by automatic titration. Relative errors are within $\pm$ 0·1% when 5 to 50 mg of metal is taken.

H. M.

1376. **Rapid deuterium determination in the presence of air.** P. H. Dutch (The Fluor Corp., Ltd., Whittier, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1532.—Samples (5 to 10 ml) of hydrogen containing 30 to 70% of ^2H are analysed gas-chromatographically, with a thermal conductivity detector. With H as carrier gas, ^2H, O and N are readily distinguished on a 4-ft. column with molecular sieve 5A packing. The sensitivity for ^2H on a 5-ml sample is 500 p.p.m.

J. P. Stern

1377. **Emission spectroscopic analysis of hydrogen - deuterium mixtures.** J. A. Parodi, W. G. Burch, L. F. Kendall and M. B. Leboeuf (Hanford Works, Richland, Wash.). *U.S. Atomic Energy Comm.*, Rep. HW-21718, July, 1951, Decl. May, 1960. 29 pp.—An emission-spectrometer procedure relating the intensities of Balmer lines to the relative concentrations of H and ^2H was calibrated for low flow rates. Isobars of true *vs.* apparent composition are given for the composition range of 89 to 100% of ^2H and for pressures of 0·7, 0·8, 0·9 and 1 torr. Experiments revealed that, with the preparation of similar calibration curves, the accurate analysis of H - ^2H mixtures could be carried out by the emission-spectrometer method.

Nucl. Sci. Abstr.

1378. **Contribution to the analysis of alkali metals.** H. Koch (Inst. f. Angew. Radioaktivität, Leipzig). *Kernenergie*, 1960, **3**, 315–320 (in German).—By using light isotopes, the techniques of separating the alkali metals are checked. The chloroplatinic, perchlorate, and Kalignost (Na tetraphenylborate) methods do not give satisfactory analytical results. Also, in regions where apparently good values are obtained, satisfactory separations of the different alkali metals are not possible. This is true also for Na - Li separations with amyl alcohol, and ether - alcohol - HCl mixtures. None of these methods gives adequate results and they are not useful for separating mixtures which contain isotopes of alkali metals. By isotopic dilution analysis, Na can be determined in alkali-metal mixtures in a simple manner. An exact quant. determination of Na in complex materials is also possible, as is the determination of $< 10\%$ of sodium impurities in potassium hydroxide or potassium chloride.

Nucl. Sci. Abstr.

1379. **Polarographic determination of alkali metals in aqueous - alcoholic solution without supporting electrolyte.** G. M. Panchenkov, E. M. Kuznetsova and N. B. Akshinskaya (Lomonosov Univ., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 424–426.—The limits of useful concn. of alkali-metal chlorides were 0·0005N to 0·0070N in aq.

medium and 0·0020N to 0·0140N in aq. alcoholic medium (95% or 75% methanol, or 75% ethanol). A more negative value for $E_{\frac{1}{2}}$ was obtained in comparison with corresponding potentials observed in the presence of a supporting electrolyte. For example, the $E_{\frac{1}{2}}$ was − 3·82 V for Li^+, − 3·12 V for K^+, and − 3·08 V for Na^+, all in aq. soln., but a linear relationship between the height of the waves and the concn. was still obtained for the given concn. range. The most promising polarograms were obtained with a Li - K mixture in 95% methanol without a supporting electrolyte: two separate waves were shown. There is no separation of this mixture in aq. soln. K. R. Cook

1380. **Direct titration of potassium with tetraphenylborate. Amperometric equivalence-point detection.** D. L. Smith, D. R. Jamieson and P. J. Elving (Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1253–1257.—Tetraphenylborate ions are electrochemically oxidised at the graphite electrode. Potassium may be determined in soln. of pH 2 to 6 by titration with sodium tetraphenylborate soln. (≃ 3%) by means of a calomel - graphite electrode system at pH ≃ 5 (acetate buffer), with an applied voltage of + 0·55 V on the graphite electrode. Results for known soln., ≮ 5 mM in K, are within 1% of the amount added. The major interferences with the method are NH_4^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg^{2+} and nitrogen bases that react with sodium tetraphenylborate. Large amounts of SO_4^{2-}, Cl^-, PO_4^{3-} and acetate do not interfere. The method has been successfully applied to samples of limestone, glass and silica brick. T. R. Andrew

1381. **Flame-photometric determination of small amounts of rubidium in silicates.** E. A. Fabrikova (Inst. of Mineral., Geochem. and Crystallochem. of Rare Elements, Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 427–430.—The effect of Cs, K, Na and Li on the intensity of rubidium emission (at 894·4 mμ) in the air - acetylene flame was studied, and it was found that the emission can be intensified and stabilised by the addition of K. Add conc. H_2SO_4 (0·4 ml), HF (15 ml) and HNO_3 (2 to 3 drops) to the mineral sample (0·5 to 1·0 g) and heat the mixture at 70° to 80° until H_2SO_4 fumes appear. Cool the product, add H_2O (2 ml) and conc. H_2SO_4 (0·1 ml) and again heat to fuming; evaporate for the third time with H_2O. Add H_2O (25 to 30 ml) to the residue, heat until no more will dissolve and dilute the soln. plus residue to 50 ml. Filter off the residue and reject the first portion of filtrate. Add K_2SO_4 soln. (25 mg of K per ml) (2·5 ml) to the filtrate (20 ml), dilute it to 25 ml, and measure the extinction at three different wavelengths—8 to 10 mμ above and below the rubidium line and on the rubidium line at 794·8 mμ. Simultaneously measure a standard soln. of rubidium sulphate with K_2SO_4 added at the same concn. The rubidium content is calculated from a given equation. This method allows of the determination of Rb in the parts per 10^5 and 10^6 range in a sample without a preliminary separation of Cs, K, Na, Li, Ca, Sr, Mg, P or Fe. The experimental error is 15%. K. R. Cook

1382. **Hexachlorotellurous acid as a precipitant for caesium.** H. A. C. Montgomery (Water Pollut. Res. Lab., Stevenage, Herts., England). *Analyst*, 1960, **85**, 687–688.—In the determination of radioactive caesium it is usually weighed as $CsClO_4$ or Cs_2PtCl_6 after separation from K and other elements. Since the caesium and potassium salts of hexachlorotellurous acid have widely different solubilities in HCl, a rapid and convenient method for pptn. of Cs with relatively slight co-pptn. of K has been developed. Hexachlorotellurous acid reagent is added to the soln. of Cs in 11 to 12N-HCl. The reagent is prepared by dissolving 10 g of TeO_2 in conc. HCl, evaporating the soln. to a small bulk and diluting the cooled residue to 100 ml with 11 to 12N-HCl. Since the ppt. of Cs_2TeCl_6 is appreciably sol. in HCl, washing is kept to a minimum. The ppt. decomposes slowly in the presence of moisture, especially when in contact with a metallic surface, but samples on aluminium counting planchets may be protected for storage by moistening them with a 5% soln. of polystyrene in benzene and evaporating the solvent to give an impervious film. A. O. Jones

1383. **Co-precipitation of caesium with thallium picrate.** I. M. Korenman, P. A. Ganichev and I. I. Melekhonova. *Trudy Khim. i Khim. Tekhnol.*, 1959, (1), 85–89; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 72,970.—The isotope ^{134}Cs is used to study the co-pptn. of Cs^+ with Tl with an aq. picric acid soln. The $TlNO_3$ soln. (0·6 ml, containing 5 mg of Tl^+ and 40 μg of Cs^+) and 1% aq. picric acid soln. (1 ml) were stirred in a centrifuge tube for 30 min., and the ppt. was centrifuged off, washed (× 2) with s-butyl alcohol and dissolved in 0·7 ml of HNO_3 (1:1); the co-pptd. Cs was determined radiometrically. The influence on the co-pptn. of temp., time of standing of the ppt. in contact with the mother liquor, rate of mixing the reagents and other factors was studied. The rate of mixing the reagents and the time of standing of the ppt. have no effect on the co-pptn. of Cs. At increased temp., Tl picrate dissolves to a considerable extent, causing a reduction in the total amount of co-pptd. Cs from 58 to 29%; the amount of Cs co-pptd. per mg of ppt. decreases from 2·8 to 2·2 μg. The addition to the sample of Cr^{3+}, Fe^{3+}, starch, agar and gelatin does not affect the co-pptn. A small amount of Cs is co-pptd. with freshly pptd. Tl picrate. It is concluded that the co-pptn. is isomorphous in nature. The pptn. of Tl with an aq. picric acid soln. does not separate Tl from Cs, because of the co-pptn. of Cs and the considerable solubility of the picrate. C. D. Kopkin

1384. **The use of picrolonic acid for the detection of traces of copper with the electron microscope.** E. Wiesenberger (Freie Univ., Berlin). *Mikrochim. Acta*, 1960, (5–6), 946–960 (in German).—Electrodeposition of Cu (0·005 to 0·00005 μg), followed by reaction with picrolonic acid, yields characteristic crystals which are clearly identified by the electron microscope. Full analytical details are given, together with 17 electron micrographs. P. D. Parr-Richard

1385. **Lead diethyldithiocarbamate as a specific reagent for copper.** I. Adamiec. *Rudy i Metale Nieżalazne*, 1960, **5** (10), 409–412 (in Czech).—Copper is detected in certain metals by dissolving them in a suitable mineral acid, adding a $CHCl_3$ soln. of Pb diethyldithiocarbamate and measuring the extinction of the organic layer. For Co, Zn and Al, HCl is used; for Pb, H_2SO_4; and for Pb with Ni, HNO_3 followed by H_2SO_4. The time required for a determination is 20 min. and the limit of detection is 0·2 μg of Cu per ml of acid soln. P. Glover

1386. **Separation of copper as cuprous tetraphenylborate.** D. G. Davis (Div. of Sci., Louisiana State Univ., New Orleans, U.S.A.). *Anal. Chem.*, **1960, 32** (10), 1321–1322.—*Procedure*—To 75 ml of sample soln. (containing 2 to 60 mg of Cu and 2 to 4 drops of conc. HCl) are added 10 ml of 0·1M-Na tetraphenylborate (**I**) and 10 ml of 0·1M-ascorbic acid (**II**). The mixture is set aside for 0·5 to 24 hr. and the ppt. is filtered off and washed with a soln. containing 10 ml of **I** and 10 ml of **II** and 250 ml of water. The ppt. cannot be weighed as such but may be dissolved in HNO_3 and the copper determined by titration with 0·005M-EDTA (disodium salt). Interferences by 11 metal ions are discussed. T. R. Andrew

1387. ***o*-(Toluene-*p*-sulphonamido)aniline (T-sulphonamidine) as a new type of analytical reagent. Gravimetric determination of cupric ion.** J. H. Billman, N. S. Janetos and R. Chernin (Dept. of Chem., Indiana Univ., Bloomington, U.S.A.). *Anal. Chem.*, **1960, 32** (10), **1342–1344.**—In the course of a study of sulphonamides as reagents it was found that *o*-(toluene-*p*-sulphonamido)aniline was a specific precipitant for Cu^{II}; pptn. is quant. in the pH range 6·2 to 8·5. Interference is limited to ions pptd. at this pH and to Ag^+, which is reduced by the reagent. Most interferences are eliminated by working in tartrate soln. T. R. Andrew

1388. **Determination of a small amount of copper by titration with iodate.** I. L. Bagbanlÿ. *Trudÿ Inst. Khim., AN, Azerbaidzh. SSR,* **1959, 17,** 83–97; *Ref. Zhur., Khim.*, **1960,** (15), Abstr. No. 61,029.—Add H_2SO_4 or HCl to a test soln. containing Cu^+ (0·08 to 3·8 mg), ensuring that the acid concn. after the addition of the precipitating agent will be 2N, heat on a water bath, add an excess of 2·5% $NH_4[Cr(SCN)_4(NH_3)_2].H_2O$ soln. (freshly prepared), set aside in a water bath until the supernatant liquid becomes clear, and then filter. Wash the ppt. with hot water until the rose tint is discharged, transfer the filter with the ppt. into the vessel in which the pptn. has been carried out, add hot 5% NaOH soln. (5 ml), and heat on a water bath until the ppt. is completely decomposed. Then add conc. HCl (at the end of the titration the soln. must be 4 to 4·5N with respect to HCl), cool, add benzene (10 ml), and titrate with 0·005 to 0·1N-KIO_3 until the benzene layer is decolorised; Fe^{2+} do not interfere with the determination, but Fe^{3+} do, and may be masked by 15% KF soln. The method may be used for determining Cu in steel and cast iron. K. R. Cook

1389. **Catalytic determination of microgram amounts of copper by amperometric measurements.** K. Czarnecki (Dept. of Inorg. Chem., Univ. Łódź, Poland). *Chem. Anal., Warsaw,* **1960, 5** (3), **377–382.**—Copper is a catalyst for the reaction $2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$. Under specified conditions, the time of reaction is inversely proportional to the concentration of Cu^{2+}. With two-electrode amperometry to follow the rate of reaction, 6 to 30 μg of Cu can be determined by measuring the half-times of reaction (*i.e.*, the time required for the current to fall to one-half of its original value). The precision is claimed to be $\simeq$ 2%. The effects of temperature variation were noted, but not evaluated quantitatively. P. Brych

1390. **Photometric determination of copper in the presence of nickel and cobalt.** L. B. Kristalëva and R. D. Tresnitskaya. *Ucheb. Zap. Tomskiĭ Univ.*, **1959,** (29), 126–129; *Ref. Zhur., Khim.*, **1960,** (16), Abstr. No. **65,068.**—The method is based on preliminary separation of Ni and Co with dimethylglyoxime, followed by the photometric determination of Cu with Na diethyldithiocarbamate. K. R. Cook

1391. **Potentiometric investigation of several precipitation and complexing reactions for silver in strongly alkaline solution.** G. Facsko and R. Minges (Polytech. Inst., Timisoara, Romania). *Talanta*, **1960, 5** (2), 102–107 (in German).—Silver *p*-sulphamoylbenzoate can be dissolved in alkali and the Ag titrated potentiometrically with standard KCl, KBr, KI or KCN soln., with silver and satd. calomel electrodes and a KNO_3 salt bridge. The end-point is affected by the alkalinity of the soln.; to prevent this from changing during the titration, alkali must be added to the titrant. An error due to the oxidation of KI by dissolved O in the test soln. can be prevented by the addition of Na_2SO_3. The most accurate results are obtained with KCN. W. T. Carter

1392. **Determination of small amounts of silver in developed photographs.** N. N. Shishkina (Optical Inst., Leningrad). *Zhur. Anal. Khim.*, **1960, 15** (4), **431–436.**—Place punched-out circles of film (diam. 5 mm) in quartz tubes and add 3N-HNO_3 to each tube (the amounts recommended for the dissolution of various possible silver contents are tabulated); the final HNO_3 concn. in the test soln. should be $\not>$ 0·1N. Heat the mixture, then dilute the cooled soln. and to an aliquot add 0·01% ethanolic *p*-dimethylaminobenzylidenerhodanine soln. (**I**) (0·4 ml of **I** per 5 ml of silver soln.). Stir the soln. without shaking and measure the extinction at 470 to 480 mμ. Take readings every 1·5 to 5 min. over a period of 10 to 20 min.; keep the soln. in the dark between readings, and refer the results to calibration curves. Keep the extinction values within the limits 0·08 and 0·2, which correspond to 0·1 to 1·0 μg of Ag per ml. This method permits of the determination of 0·04 μg of Ag per ml, *i.e.*, 5×10^{-5} g of Ag per 100 sq. cm of test layer. The accuracy is from 1 to 6% at concn. of 0·15 to 2·0 μg of Ag per ml. The reproducibility of the results is within 4%. K. R. Cook

1393. **New spot test for auric gold with *NN'*-di-(2-naphthyl)-*p*-phenylenediamine.** J. C. Soriano and E. Jungreis (Hebrew Univ., Jerusalem, Israel). *Talanta*, **1960, 5** (2), 127–128 (in English).—Tervalent gold gives a deep-red meriquinonoid compound with *NN'*-di-(2-naphthyl)-*p*-phenylenediamine at pH 3 to 8. The limit of identification is 0·1 μg of Au^{III} and the limit of dilution is 1 in 5×10^5; Fe^{III}, Ce^{IV} and Os^{VIII} interfere, but Fe^{III} can be masked with KF, and OsO_4 can be removed by boiling. Interference from $Fe(CN)_6^{3-}$ and SO_3^{2-} can be prevented by boiling with H_2O_2, that of MnO_4^- by reduction with As_2O_3 and Na_2CO_3, and that of S^{2-} by pptn. with $ZnCO_3$. W. T. Carter

1394. **Spectrophotometric determination of beryllium with 2-phenoxyquinizarin-3,4'-disulphonic acid.** E. G. Owens, II, and J. H. Yoe (Pratt Trace Analysis Lab., Dept. of Chem., Univ. Virginia, Charlottesville, U.S.A.). *Anal. Chem.*, **1960, 32** (10), **1345–1349.**—At pH 6·0, 2-phenoxyquinizarin-3,4'-disulphonic acid reacts with Be to give a stable violet

complex (extinction $\simeq$ 0·4 at 550 mμ for 0·3 p.p.m. of Be in a 1-cm cell). The interference of most elements is eliminated by ion exchange, mercury cathode electrolysis, or addition of EDTA (calcium salt). Results are presented for the determination of Be in beryl, aluminium, copper alloys and steel. T. R. Andrew

1395. **Spectrographic determination of traces of beryllium in ores by means of a sifter electrode.** J. Czakow and Z. Walewska (Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw,* **1960, 5** (3), **369–375.**—A semi-quant. extrapolation method, in which an internal standard is used, is described. The samples are held in a copper sifter-electrode, excitation is by a Feussner condensed spark and background correction is applied. The determinable range is 1 to 20 p.p.m. of Be and the coeff. of variation is $\pm$ 8·2%. P. Brych

1396. **The photo-neutron method for determining beryllium in ores.** F. I. Dvorechenskiĭ, I. P. Koshelev, B. M. Naĭdenov, S. N. Neuchesov, O. V. Shishakin and L. I. Shmonin. *Trudy̆ Kazakhsk. Nauch.-Issled. Inst. Mineral. Sy̆r'ya,* **1959,** (1), **204–211**; *Ref. Zhur., Khim.,* 1960, (18), Abstr. No. **73,047.**—A method and apparatus are described for the photo-neutron determination of Be in ores by the reaction ^{9}Be (γ, n) ^{8}Be; ^{124}Sb (60 to 75 mC) is used as a γ-source, and BF_3 proportional counters connected with an adapted B–2 radiometer as neutron detector. The sensitivity of the method is 5 $\times$ 10^{-3} % of BeO with measurement for 10 min. on a sample of 50 to 180 g. The method has no upper sensitivity limit. The accuracy of the determination is independent of the presence of impurities (except B), moisture, and the degree of grinding of the sample. The influence of B is eliminated by means of a cadmium screen, but the sensitivity is then decreased by 25 to 30%. The method is simple and highly efficient. C. D. Kopkin

1397. **Ion exchange and other chemical methods for beryllium-base alloys.** S. Kallmann, R. Liu and H. Oberthin (Ledoux and Co., Teaneck, N.J.). *U.S. Atomic Energy Comm.,* Rep. WADC–TR–59–**325,** May, 1959. **39 pp.**—Procedures are described for both cation- and anion-exchange resins which enable all elements present in beryllium alloys to be determined in successive steps on one sample portion. The elements covered in the range of 0·1 to 10% are Cu, Al, Ni, Co, Ce, Ag, Au and Pd. Nucl. Sci. Abstr.

1398. **Determination of fluorine in beryllium.** J. F. W. Smith and R. H. A. Crawley (Atomic Power Div., English Electric Co. Ltd., Whetstone, Middlesex, England). *Anal. Chim. Acta,* **1960, 23** (4), **345–350** (in English).—Fluoride is separated from Be^{2+} by steam-distillation from H_2SO_4 at 140° and subsequently determined photometrically in the distillate by the Zr^{IV} - sodium 4,5-dihydroxy-3-(4-sulphophenylazo)naphthalene-2,7-disulphonate (SPADNS) method of Bellack and Schouboe (*Anal. Abstr.,* 1959, **6**, 2794). T. R. Andrew

1399. **Spectrographic determination of phosphorus in beryllium oxide.** I. A. Berezin and K. V. Aleksandrovich. *Zhur. Anal. Khim.,* **1960, 15** (4), **509–510.**—Spectrograph ISP–22 is used with a slit width of 0·02 mm, a 14-amp. interrupted a.c. arc as light source, a burning time and interruption of 0·5 sec., and a total exposure time of 3 min. The standards containing 0·001 to 0·1% of P are prepared by grinding calcium orthophosphate with BeO. The sample is introduced into the light source on a moving cylindrical graphite electrode (length 80 mm, diam. 40 mm) rotating at 1 r.p.m.; the linear transporting velocity of the electrode is 0·2 cm per sec. The upper electrode is a carbon rod (diam. 6 mm) and the electrode gap is 2 mm. Type-III spectrographic plates are used. The sensitivity of the determinations is 0·001% and the reproducibility of the results is $\pm$ 6%. K. R. Cook

1400. **Arsenate - iodimetric method of determination of magnesium in the presence of iron and aluminium.** G. B. Shakhtakhtinskiĭ and G. A. Aslanov. *Azerbaidzh. Khim. Zhur.,* **1959,** (4), **101–104**; *Ref. Zhur., Khim.,* **1960,** (16), Abstr. No. **65,078.**—In the method described, Al^{3+} and Fe^{3+} ($\ngtr$ 0·03N) are complexed with citric acid, Mg is pptd. by Na_3AsO_4, and the AsO_4^{3-} in the ppt. are determined iodimetrically. K. R. Cook

1401. **Determination of magnesium and aluminium in zinc-based die-casting alloys.** L. Bloch (H. J. van der Rijn, N. V. Res. Lab., Naarden, Netherlands). *Anal. Chim. Acta,* **1960, 23** (3), **233–239** (in English).—*Determination of Al*—The alloy (turnings or drillings) (5 g) is dissolved in dil. HNO_3; Cu and Pb are removed by electrolysis, and the soln. is made up to 500 ml. An aliquot (100 ml) is treated with 20 ml of 50% aq. NH_4NO_3 soln. and the soln. is neutralised to pH 3. The soln. is cooled and poured, with stirring, into a beaker containing 75 ml of water, 20 ml of 50% aq. NH_4NO_3 soln. and 10 ml of aq. NH_3 (sp. gr. 0·91). This gives a ppt. substantially free from Zn. The ppt. is filtered off, washed and dissolved in warm acid. After neutralisation to pH 3 the Al is re-pptd. as described above, but with 8 ml instead of 10 ml of aq. NH_3. The ppt. is filtered off, dried and ignited to constant weight. *Determination of Mg*—A similar sample (10 g) is dissolved in dil. HCl; Cu, if present, is dissolved by adding a few drops of HNO_3. The Mg is pptd. as $MgNH_4PO_4.6H_2O$ in the usual manner, filtered and washed. The ppt. is dissolved in the minimum of warm 0·5N-HCl, and the soln. is passed through an ion-exchange column (Dowex 1–X8) which is washed with water. The percolate and washings, now free from PO_4^{3-}, are evaporated to $\simeq$ 25 ml, and buffered to pH 8 to 10. The Mg is titrated with 0·02N-EDTA (disodium salt), with Eriochrome black T (**I**) or methylthymol blue (**II**) as indicator. It is important to clean the titration flask with boiling HCl (1 : 1) after each determination to remove residual traces of **I** which give premature transient end-points. Soln. of **II** do not keep for more than a fortnight, and should be stored in a cool place in a dark bottle. A small amount of Zn is co-pptd. with the Mg and should be allowed for in precise work. H. M.

1402. **Complexometric determination of thorium and zirconium in magnesium alloys.** R. S. Volodarskaya. *Zavod. Lab.,* **1960, 26** (8), **925–927.**—*Determination of Th in the absence of Zr*—The sample (1 g) of magnesium alloy is dissolved in 30 ml of HCl (1 : 1), the soln. is diluted with 60 to 70 ml of water, aq. NH_3 is added until a lilac-blue colour is obtained with Congo red paper, 1 ml of 0·1% arsenazo soln. is added, and the soln. is titrated with 0·025N-EDTA (disodium salt) to a pink end-point. *Determination of Th in the presence*

of Zr—The soln. of the alloy in HCl is treated with 2 to 3 ml of 1% benzenearsonic acid soln. and boiled for 4 to 5 min. to precipitate the Zr. The cooled soln. is diluted to 200 ml and set aside until the ppt. has coagulated. A portion (100 ml) of the filtered soln. is neutralised with aq. NH_3 and titrated as described above. *Determination of Zr in the absence of Th*—The sample (1 g) is dissolved in 40 to 50 ml of HCl (1:1) and the soln., after dilution with 20 to 25 ml of water, is treated with 0·025N-EDTA (disodium salt) so that there is an excess of 4 to 5 ml. The soln. is boiled for 2 to 3 min., then cooled to between 40° and 50°, and treated with aq. NH_3 until a lilac colour is obtained with Congo red paper. After addition of 2 ml of 10% sulphosalicylic acid soln. the excess of EDTA is titrated with 0·025N-$FeCl_3$ to the colour change from yellow to pink. The method is satisfactory in the presence of Ag, Cd, Zn, Al, Mn, Nd, La and Pr. In the presence of Th, the Zr is pptd. from a 10% HCl soln. by benzenearsonic acid in an amount five times that of the Zr. The separated ppt. is made soluble by fusion. The EDTA soln. is added in excess to a hot 20% HCl soln., which is then boiled for 2 to 3 min. G. S. SMITH

1403. **Photometric determination of calcium in magnesium alloys, with preliminary removal of magnesium by alkali in the presence of EDTA (disodium salt).** L. Ya. Polyak. USSR Pat. No. 127,069 (10.3.1960).—With arsenazo (**I**) at pH 12·5 to 13·0, calcium forms a soluble blue-violet complex; the sensitivity is 0·04 µg of Ca per ml. The colour is developed instantaneously and is stable for at least 3 days. The max. absorption is at 570 mµ. The intensity is proportional to the concn. of Ca in the range 0·01 to 0·1 mg per ml, and the max. colour is developed at pH 12·0 to 13·0. In determining Ca in the presence of Mg, the Mg is pptd. with NaOH in the presence of EDTA (disodium salt), the EDTA in the filtrate is oxidised by boiling with H_2O_2, and Ca is determined colorimetrically with **I**. No interference is caused by Al, Zn or residual Mg. The method can be used to determine 0·01 to 2·0% of Ca in alloys. C. D. KOPKIN

1404. **Releasing effects in flame photometry. Determination of calcium.** J. I. Dinnin (U.S. Geol. Survey, Washington, D.C.). *Anal. Chem.*, 1960, **32** (11), 1475–1480.—Methods are described for overcoming the depressive effects on Ca, due to sulphate, phosphate and aluminate, by the addition of releasing cations; Sr^{2+}, La^{3+}, Nd^{3+}, Sm^{3+} and Y^{3+} completely release the flame emission of Ca, while Mg^{2+}, Be^{2+}, Ba^{2+} and Sc^{3+} release most of the Ca emission. The mechanism of the interference and releasing effects, *i.e.*, the preferential formation of certain compounds in the flame, is explained on the basis of chemical equilibria in the droplets of soln. evaporating in the flame. The results presented show a greater flexibility in the choice of releasing agent than was previously possible. A releasing agent may be selected on the basis of molar effectiveness, background emission, or availability and cost of reagent. The method is applied to the determination of Ca in silicate rocks without using separation techniques, and results are in good agreement with those of a chemical method of analysis. C. B. BAINES

1405. **Determination of traces of nitrogen in metallic calcium.** C. Den Tandt (Inst. Inter-univ. des Sciences Nucléaires, Brussels). *Mém. Sci. Rev. Métall.*, 1960, **57** (9), 676–682.—Calcium purified by vacuum sublimation is very reactive; an apparatus is described in which a soln. of the sample is safely prepared, with cooling, in an inert atmosphere. *Procedure*—After introduction of calcium (10 g) purge the apparatus with a rapid stream of dry Ar. Reduce the flow of gas and add the following soln. in the order given—a mixture (1:1) of HCl (1:3) and twice-distilled glycerol (5 ml), HCl (1:3) (15 ml) and sufficient HCl (2:1) to complete dissolution of the sample. Dilute to 250 ml and transfer 25 ml to a semi-micro Kjeldahl apparatus. Add 15 ml of 40% NaOH soln. and steam-distil, trapping the NH_3 in 20 ml of 0·02N-HCl in a 100-ml flask. When the receiver is three-quarters full add 5 ml of Nessler reagent, dilute to 100 ml and after 10 min. measure the extinction at 450 mµ. Compare with a standard curve. The method is valid for up to 200 µg of N per 100 ml, with a reproducibility of ± 4 µg. A. J. BENNETT

1406. **Photometric determination of strontium.** A. S. Karnaukhov, M. Mizera and R. Palaush (Higher Pedagog. School, Prague). *Zhur. Anal. Khim.*, 1960, **15** (4), 502.—*Procedure*—Set aside a mixture of test soln. (< 1·75 mg of Sr per ml) (5 ml) and 0·05N-dilituric acid (**I**) (5 ml) for 15 min. With higher concn. of Sr use more **I**. Filter the mixture and measure the extinction of the filtrate at 420 mµ, in a 0·5-cm cell. Construct a calibration curve. With low concn. of Sr (up to 2 mg per ml) the max. error is 2%, but this increases with increase in concn.; certain cations (NH_4^+, K, Sn, Fe, Cr, Cd, Cu, Ca, Ba, Zn, Co, Ni, Hg, Ag and Pb) interfere. K. R. COOK

1407. **Flame-photometric determination of barium and sulphate: an improved technique.** D. C. Cullum and D. B. Thomas (Colgate-Palmolive Ltd., 371 Ordsall Lane, Manchester, England). *Analyst*, 1960, **85**, 688–689.—In a method previously reported (*Ibid.*, 1959, **84**, 113) for the determination of SO_4^{2-} in detergents, the SO_4^{2-} were pptd. as $BaSO_4$, which was separated by centrifuging and suspended in 1% starch soln. for analysis by flame photometry. In this modification the $BaSO_4$ is dissolved in EDTA soln. (ammonium salt). The sample (≡ 0·1 to 0·2 mg of SO_4^{2-}) in aq. soln. is treated with conc. HCl and diluted to 100 ml. A 5-ml portion is treated with 5 ml of 1% $BaCl_2$ soln. and the ppt., after being washed by centrifuging, is dissolved by addition of the EDTA soln. to exactly 10 ml. A 5-ml portion of the standard soln. of H_2SO_4 or Na_2SO_4 (2000 p.p.m.) is treated identically. The E.E.L. flame photometer is set to zero with the EDTA soln., and to full deflection with the soln. containing 1000 p.p.m. of SO_4^{2-}, and the sample is then examined. The SO_4^{2-} (%) is the scale reading divided by five times the sample wt. The sample must be freed from surface-active matter by the method previously described; anions other than SO_4^{2-} that form insol. barium salts must be absent. A. O. JONES

1408. **Determination of barium in minerals.** A. de Sousa (Fac. of Sci., Univ. Lisbon, Portugal). *Chemist Analyst*, 1960, **49** (3), 75–76.—After dissolution of the sample, the HCl soln. (containing 0·15 to 0·3 g of Ba) is treated with $K_2Cr_2O_7$ and the $BaCrO_4$ is collected by filtration; an EDTA titration completes the determination. *Procedure*—Dissolve the ppt. of $BaCrO_4$ in 100 ml of HCl (1:1) containing 2 g of KI and dilute to 1 litre. Transfer a 500-ml aliquot to each of two beakers and precipitate the Cr with aq. NH_3. Filter, wash, and

evaporate the filtrates and washings to 200 ml. To one beaker add 200 ml of ethanol, 8 to 12 drops of 0·1% metalphthalein soln. (phthalein complexone) (Anderegg *et al.*, *Anal. Abstr.*, 1954, **1**, 1180) and 2 ml of conc. aq. NH_3, and titrate with 0·1M-EDTA (disodium salt) until colourless. If pptn. occurs and obscures the end-point, titrate the soln. in the second beaker, but add the ethanol just before the end-point. Results are slightly higher than those obtained gravimetrically.

P. D. PARR-RICHARD

1409. **Simultaneous determination of barium and strontium in silicate rocks, by the method of addition, by emission spectroscopy in an electric arc.** V. Gabis (Lab. de Min.-Crist., Fac. des Sci., Paris). *Compt. Rend.*, 1960, **251** (2), 232–234.—The technique of successive additions has been used for samples in which the Ba and Sr were in the form of chlorides, sulphates and calcined oxides. The most reproducible results were obtained when the elements were in the form of sulphates and the addition was made by impregnation of the graphite. A d.c. arc was used with c.d. 4·5 amp. for clays after attack by HF - HCl or HF - H_2SO_4 and 7·5 amp. for calcined clays. The relative intensity of the lines due to Sr (4607·33 A) and Ba (4554·04 A) varies linearly with the concn. of these added metals provided that the concn. of Ba is $\not> 150 \times 10^{-6}$. The lines Mg (5183·62 A) or K (5782·60 A) (for additions as chloride diluted with KCl) are used as internal reference lines.

J. H. WATON

1410. **Micro-determination of zinc by chromatography and colorimetry.** F. Burriel-Martí and R. Gallego Andreu (Dept. Chim. Anal., C.S.I.C., Madrid, Spain). *Mikrochim. Acta*, 1960, (5-6), 912–916 (in French).—A chromatographic separation of 5 μg of Zn from Cu (150 μg), Fe (150 μg), Mn (1 μg), Co (25 μg), Ti (25 μg), Ni (25 μg), Cr and Pb is described. By using Whatman No. 1 paper (purified by washing with 1% aq. EDTA and water) and butanol - 2N-HCl (1:1) as solvent, an R_F value of 0·75 is obtained for Zn; values for the other metals are, respectively, Cu 0·24, Fe 0·20, Mn 0·10, Co 0·08, Ti 0·00, Ni 0·05, Cr 0·00, and Pb 0·00 (some tailing). The spot due to Zn is located with dithizone soln. (0·01% in CCl_4) (sensitivity 1 μg of Zn) and the Zn dithizonate is exhaustively extracted with 2N-HCl before the colorimetric determination with dithizone.

P. D. PARR-RICHARD

1411. **Spot-test detection of cadmium in plating.** J. G. Sabo (54 Bergen Avenue, Clifton, N.J., U.S.A.). *Chemist Analyst*, 1960, **49** (3), 78.—The test surface is treated with 1 to 2 drops of satd. aq. NH_4NO_3 soln. and, after exactly 45 sec., the liquid is adsorbed on to filter-paper. Addition of 1 drop of 10% Na_2S soln. to the spot gives a yellow stain in the presence of Cd. Zinc, Mn and Pb are only slightly attacked and Be, Ti, Zr, Cr, Mo, Fe, Co, Ni, Cu, Ag, Hg, Al, Sn, Sb and Bi are not attacked within 45 sec.

P. D. PARR-RICHARD

1412. **New rapid gravimetric method for the determination of cadmium.** I. Grecu (Fac. Pharm., I.M.F., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1959, **10** (2), 295–298.—The proposed method is based on the formation of a complex of Cd^{2+} with piperazine in the presence of excess of NH_4SCN. *Procedure*—The sample ($\simeq$ 10 to 30 ml) is treated with 2 g of NH_4SCN, then acidified with 2 or 3 drops of acetic acid, and 25 ml of a 4% soln. of piperazine is added in the cold. The pptd. $[Cd(C_4H_{10}N_2)](SCN)_2$ is filtered off and washed successively with a soln. containing 0·2% each of piperazine and NH_4SCN, a soln. containing 0·04% of each, 1% piperazine soln. in ethanol - ether (1:3) (5 × 2 ml), and ether containing 0·1% of piperazine (4 × 2 ml), and vacuum-dried. The coeff. of variation is ± 0·25%, and the sensitivity is 80 μg per ml. Alkali and alkaline-earth metals, Hg^{2+} and Mn^{2+} do not interfere, but Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Al^{3+} and Cr^{3+} do.

H. SHER

1413. **Co-precipitation of small amounts of cadmium with certain metal hydroxides.** V. I. Plotnikov. *Zhur. Neorg. Khim.*, 1959, **4** (12), 2775–2778; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 46,970.—The radioactive isotope ^{115}Cd is used to study the co-pptn. of small amounts of Cd with the hydroxides of Be, Al, Cr, Ti, Fe, Bi and Pb as a function of the concn. of aq. NH_3, the amount of hydroxide pptd., the temperature, the time of standing of the ppt., and other factors. The co-pptn. of Cd with $Fe(OH)_3$ decreases with increase of the NH_4^+ concn. On increasing the Cd content of the soln., the percentage co-pptn. decreases, but the absolute amount of Cd in the ppt. is increased. The amount of co-pptd. Cd also increases with increase of the amount of $Fe(OH)_3$; at pH 6·9 to 9·7, in the absence of ammonium salts, 4 μg of Cd is almost completely co-pptd. with 7 mg of Fe^{3+}. Increasing the time of standing of the ppt. from 30 min. to 30 hr. causes a slight decrease in the co-pptn. only in alkaline medium. Increase of temp. decreases the co-pptn. The co-pptn. increases in the order Pb^{2+}, Be^{2+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Fe^{3+} and Ti^{4+}. There is practically no co-pptn. with $Pb(OH)_2$. The maximum co-pptn. is at pH 7 to 8, which corresponds to complete pptn. of $Cd(OH)_2$ when aq. NH_3 is added to pure soln. of Cd salts. It is shown that the co-pptn. of Cd with the hydroxides of the metals named is due to adsorption.

C. D. KOPKIN

1414. **Application of the molten zinc electrode to the spectrographic determination of small amounts of cadmium in zinc.** B. Czerny-Hołyńska (Dept. of Metallurgy of Non-Ferrous Metals, Acad. of Mining and Metallurgy, Cracow, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 383–388.—By using a molten zinc electrode similar to that of Frederickson and Churchill (*Anal. Abstr.*, 1954, **1**, 2063) the effects of non-homogeneity of samples were nullified, and as little as 0·004% of Cd could be determined, as compared with 0·05% with solid electrodes. The best results were obtained at 450°; zinc vapours interfere at higher temp.

P. BRYCH

1415. **Detection of mercuric ions with potassium antimonyl tartrate.** E. Chinoporos (Suffolk Univ., Boston, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1364.—When a soln. of potassium antimonyl tartrate (4%) (2 ml) is added to a soln. containing Hg^{II} [0·1% as $Hg(NO_3)_2$] (3 ml) and the mixture is made alkaline with aq. NH_3, a grey - black ppt. is produced. This is not formed by 18 other common ions examined and the reaction is suggested as a qualitative test for Hg^{II}.

T. R. ANDREW

1416. **Volumetric determination of mercurous ions with alkali-metal ferrocyanide solutions with bromophenol blue as adsorption indicator.** H. Basińska and A. Bukowska (Dept. of Inorg. Chem., Copernicus Univ., Toruń, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 355–360.—Mercurous ions can

be titrated with K, Na or Li ferrocyanide in acid soln. (0·1N-HNO_3). Bromophenol blue as adsorption indicator gives a good colour change from purple - pink to grey - green. Cations forming insol. ppt. (*e.g.*, Zn, Pb and Cu) interfere. The accuracy on 25 to 250 mg of Hg is within 0·8% (25 titrations). P. BRYCH

1417. **Titration of mercury and nickel salts with cysteine solutions.** M. Wroński (Dept. of Chem. Technol., Univ., Łódź, Poland). *Chem. Anal., Warsaw,* 1960, **5** (3), 511–512.—Methods are described for the determination of (*i*) cysteine with $Hg(NO_3)_2$ or Na *o*-hydroxymercuribenzoate (**I**) and (*ii*) Hg^{2+} or Ni with cysteine. *Procedure for* (*i*)—To a soln. of cysteine (1 to 70 mg) add 5 ml of N-NaOH and 0·2 ml of 0·1% ethanolic dithizone, dilute to 100 ml and titrate with 0·005N to 0·05N-$Hg(NO_3)_2$ or **I** to a red end-point. The accuracy is 0·2 to 1%. *Procedure for* (*ii*)—To 100 ml of a soln. containing < 50 mg of Hg^{2+} add 5 ml of N-aq. NH_3, clear with 5 ml of 3% Na_2SO_3 soln., add 1 ml of thiofluorescein soln. (0·1% in 0·2N-aq. NH_3) and titrate with cysteine soln. (0·03N in 0·01N-H_2SO_4) to a permanent blue end-point. Nickel titrations are carried out similarly, except that the indicator is decolorised with **I** and an indicator correction applied. The accuracy is 0·2%. P. BRYCH

1418. **Separation and spectrophotometric determination of microgram quantities of mercury using diethyldithiocarbamate.** E. A. Hakkila and G. R. Waterbury (Univ. California, Los Alamos Sci. Lab., N. Mex., U.S.A.). *Anal. Chem.,* 1960, **32** (10), 1340–1342.—Mercuric ions are extracted with diethyldithiocarbamate (sodium salt) and CCl_4 from soln. containing EDTA (disodium salt) and KCN at pH 9·3 to 10·0. The extinction of the extract is measured at 278 mμ. Of 32 ions studied only Cu, Tl^{III} and Bi^{III} interfere seriously, but Ru should be removed by hypochlorite oxidation and volatilisation if more than 200 μg is present. The method is suitable for 1 to 50 μg of Hg. Coeff. of variation of 5% and 2% (14 determinations) are reported for 10 and 50 μg of Hg, respectively. T. R. ANDREW

1419. **Alkalimetric titration of boron after mercury-cathode and hydroxide separations of interferences.** J. C. Neace (Nuclear Div., The Martin Co., Baltimore, Md., U.S.A.). *Chemist Analyst,* 1960, **49**(3), 71–72.—Interfering elements (*e.g.*, Al and U) remaining in the soln. after mercury-cathode separation are removed by hydroxide pptn., and borate is determined in the filtrate. *Procedure*—After mercury-cathode separation, transfer the soln. to a polyethylene beaker and add 50% NaOH soln. to pH 7·5. Filter, acidify the filtrate with 2 drops of H_2SO_4 (1:4) and heat to expel CO_2. Cool, pour into a polyethylene beaker and adjust the pH to 7·3. Add mannitol (7 g) and titrate with 0·005N-NaOH to restore the pH to 7·3. The accuracy is within 0·002% for $\ngtr$ 0·1% of B. P. D. PARR-RICHARD

1420. **Photometric determination of boron by solvent extraction using monomethylthionine.** L. C. Pasztor and J. D. Bode (Jones & Laughlin Steel Corp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.,* 1960, **32** (11), 1530–1531.—*N*-Methylthionine (Azure C) is superior to methylene blue in Ducret's method for determining B (*Anal. Abstr.,* 1958, **5**, 1793) because it gives a lower reagent blank and permits a wider range (0·1 to 200 μg of B) to be determined. The extinction of the extracted complex at 658 mμ is a measure of the B content. J. P. STERN

1421. **Determination of microgram amounts of boron in complex alloys.** R. B. Golubtsova (Baĭkov Inst. of Metall., Moscow). *Zhur. Anal. Khim.,* 1960, **15** (4), 481–486.—*Procedure for nickel, cobalt and iron alloys*—With gentle heating dissolve the sample (0·05 g), consisting of finely ground turnings, in H_2SO_4 (1:2) (1 ml), cool, add 25% $(NH_4)_2S_2O_8$ soln. (0·5 ml) in the presence of 1% $AgNO_3$ soln. (0·2 ml) and boil the mixture under reflux for 15 min. Filter off the ppt. (W and Nb), wash with H_2O, dilute the filtrate to 15 ml and transfer it to a water-cooled electrolytic cell with a mercury cathode; cool to $\ngtr$ 20°. After electrolysis for 15 to 20 min., test the colourless soln. for the absence of Ni, Co, Fe or Cr (depending on the alloy). Run off the soln. from the cell, wash the mercury surface with H_2O (4 × 2·5 ml), add 40% NaOH soln. (2·5 ml) to the soln. and heat it on a water bath to coagulate the ppt. Filter off the ppt. (Ti and Zr), wash it with 1% NaOH soln. (3 × 1 ml) and discard it. Add conc. H_2SO_4 dropwise to the filtrate till the soln. is acid to Congo red paper, then add more conc. H_2SO_4 (10 ml) and HNO_3 (1:40) (2 to 3 drops) and evaporate the soln. twice to fuming (≃ 5 min.). Cool, add 0·005% carminic acid (**I**) soln. (10 ml) in conc. H_2SO_4 and set the mixture aside for at least 4 hr. [Chromotrope-2B (**II**) (C.I. Acid Red 176) or arsenazo II (**III**) may also be used as the reagent.] Measure the extinction at 575 mμ in a 10-mm cell against a blank. Calibration curves should be constructed from soln. of B-free alloys to which B has been added as a standard H_3BO_3 soln. *For titanium alloys*—Dissolve the sample (0·01 g) in H_2SO_4 (1:3) (1 ml) as described above, add 15% $(NH_4)_2S_2O_8$ soln. (0·15 ml), boil the mixture as before, and then cool it; the soln. should be clear. Add 40% NaOH soln. (2·5 ml), and heat the soln. on a water bath to coagulate the ppt. Filter off and wash the ppt. with 1% NaOH soln. (3 × 1 ml). If Cr or Ni is present electrolyse the filtrate with a mercury cathode. To the filtrate add conc. H_2SO_4 (7 ml) and conc. HNO_3 (5 drops), and evaporate twice until white fumes appear (≃ 5 min.). Cool the soln. add 0·025% **I** soln. (2 ml) or 0·01% **II** soln. (3 ml), or 0·005% **III** soln. (3 ml), and measure the extinction of the soln. in a 10-mm cell at 575 mμ (with **I**), 620 mμ (with **II**) or 640 mμ (with **III**). These methods can be used to determine 0·01% or more of B in alloys. K. R. COOK

1422. **Emission spectrographic method for determination of minute traces of boron in reactor graphite.** M. Brandenstein, I. Janda and E. Schroll. *Mikrochim. Acta,* 1960, (5–6), 935–945 (in German).—The sensitivity for the spectrographic determination of B in graphite was increased from 0·01 p.p.m. to 0·003 p.p.m., or higher, by partial ashing, use of a double arc, and volatilisation of thermostable B_4C by addition of fluoride mixtures; NaF - AlF_3 or LiF - AlF_3 was most effective. Arsenic was used as the reference material. P. D. PARR-RICHARD

1423. **Determination of boron and borides of some metals.** A. T. Pilipenko and L. N. Kugal. *Ukr. Khim. Zhur.,* 1959, **25** (6), 786–788; *Ref. Zhur., Khim.,* 1960, (15), Abstr. No. 61,079.—Decompose the borides of Ti, Zr, Nb, Ta, Cr and

W by alkali fusion in iron crucibles at 300° to 400°, then add Na_2O_2 and fuse again. Dissolve the melt with H_2O, neutralise to methyl red, precipitate the metals with a $BaCO_3$ suspension, and determine B in the filtrate by alkaline titration in the presence of invert sugar or mannitol. Decompose nickel boride with HNO_3, plus a few drops of HCl, by boiling under reflux, neutralise, precipitate Ni with Na diethyldithiocarbamate, extract with $CHCl_3$, acidify the aq. layer and boil under reflux to decompose diethyldithiocarbamic acid; determine B as described above. Decompose the borides of Mo and V by alkali fusion in nickel crucibles as described above; separate Mo, V and Ni (from the crucible) by the extraction of the diethyldithiocarbamates and determine B as described above.

K. R. Cook

1424. **Infra-red spectrophotometric determination of diborane(6) [B_2H_6], dichloroborane and trichloroborane in mixtures.** H. G. Nadeau and D. M. Oaks, jun. (Olin Mathieson Chem. Corp., New Haven, Conn., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1480–1484.—The method described is especially useful since it is rapid and relatively more sensitive than the wet chemical analysis because of the strong absorption in the infra-red region shown by boron compounds. The individual components are determined in mixtures directly from their characteristic absorption peaks—diborane(6) at 5·35 μ, dichloroborane at 8·98 μ and trichloroborane at 10·24 μ. All three components have mutual absorption bands in the regions most likely to be used for analysis and so this method is applied by using Vierordt's method (*cf.* Gillam *et al.*, "Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," pp. 185–186), with simultaneous equations to correct for overlapping absorption. The procedure has shown an over-all precision on synthetic samples of $\pm$ 2% of the three compounds in the concn. ranges studied. General interference with the analysis can be expected in the presence of compounds containing B–H and/or B–Cl linkages.

C. B. Baines

1425. **Determination of decaborane with dipyridylethylene.** E. A. Pfitzer and J. M. Seals (Univ., Pittsburgh, Pa., U.S.A.). *Amer. Ind. Hyg. Ass. J.*, 1959, **20**, 392–395.—A new reagent, 1,2-di-(4-pyridyl)ethylene (**I**), is proposed for the detection of $B_{10}H_{14}$ in xylene or in air. A 0·5% soln. in xylene was found to be best suited for the detection. **I** added to a soln. of $B_{10}H_{14}$ in xylene gives a clear pink to red soln. with an absorption peak at 515 mμ. At room temp. the colour reaches a max. intensity within 30 min., is stable for at least 1 hr., and fades slowly. The principal advantages of this reagent over quinoline (*cf.* Hill and Johnston, *Anal. Abstr.*, 1955, **2**, 3311) are increased sensitivity, more rapid colour development, and lower reagent-blank readings. Limited experiments indicate that the reagent in a gas-bubbler collecting-bottle absorbs $B_{10}H_{14}$ from current of air.

Chem. Abstr.

1426. **Use of neutron activation analysis for determining effectiveness of zone-refining techniques in the purification of aluminium.** W. D. Mackintosh (Atomic Energy of Canada, Ltd., Chalk River, Ontario). *Anal. Chem.*, 1960, **32** (10), 1272–1275.—Thirteen impurity elements in a bar of zone-refined aluminium were determined by neutron activation analysis and the results were used to indicate the degree to which the refining had reduced the concn. of these impurities in the central region of the bar.

K. A. Proctor

1427. **Chronopotentiometric study of gallium.** E. D. Moorhead and N. H. Furman (Frick Chem. Lab., Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1507–1509.—Voltammetry at const. current with a mercury-pool electrode shows that in 0·1M-KNO_3 the quarter-wave potentials ($E_{0\cdot25}$) for 10^{-3}M-$Ga(NO_3)_3$ are − 1·02 and − 0·72 V *vs.* the S.C.E. for the cathodic and anodic waves, respectively. The reaction is affected by oxide-film formation. In 7·5N-KSCN, the $E_{0\cdot25}$ for 2·5 × 10^{-3}M-$Ga(NO_3)_3$ is − 0·90 V for each wave, in good agreement with polarographic values. The cathodic transition time is nearly three times the anodic transition time. The Ga(Hg) - Ga^{III} couple in 7·5 to 10N-KSCN is reversible, and the precisely measurable anodic transition time is suitable for analytical application.

J. P. Stern

1428. **Radiochemical evaluation of solvent extraction of indium as the bromide at high concentrations.** E. B. Owens (Lincoln Lab., M.I.T., Lexington, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1366–1367.—Indium in concn. up to 0·6M can be extracted from soln. in HBr with pentan-2-one, leaving only trace quantities (6 × 10^{-5}M) of indium and much of the impurities in the acid layer.

K. A. Proctor

1429. **The chemistry of thallium and arsenic. Bromatometric determination of thallium in presence of arsenic.** E. Schulek and L. Pataki (Inst. f. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1960, (5–6), 713–720 (in German).—Boiling H_2SO_4 quant. reduces Tl^{III} to Tl^{I} in 60 min.; both As^{III} and As^{V} are unaffected; Tl (10 mg) can thus be determined by titration with $KBrO_3$ in the presence of 500 mg of As_2O_3, with an accuracy within $\pm$ 0·35%. Copper, Fe, Sn, Mg and Ag do not interfere, but V^{IV} makes recognition of the end-point difficult. *Procedure*—Warm the sample (10 ml, containing 10 mg of Tl), dilute with water (100 ml) and boil with conc. H_2SO_4 (5 ml) for 5 min. Add 20% HCl (1 ml) and KBr (0·2 g) and titrate with 0·01 or 0·1N-$KBrO_3$, with *p*-ethoxychrysoidine as indicator, to a pale-yellow end-point.

J. P. Stern

1430. **Evaluation of flame photometry for the determination of elements of the rare-earth group.** O. Menis (Oak Ridge National Lab., Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. CF-52-8141, 1959. 20 pp.—Flame spectra are presented of all rare-earth elements, except Ce and Pm, and of the closely related elements, Sc and Y. The precise wavelength and relative spectral intensity of each line and band, as well as the width of all bands, are tabulated. In addition, the major bands and lines of each element are listed separately, together with the half-band width of all bands. Also included in this tabulation are the relative spectral interferences of other elements of the group studied which interfere with the emissivity measurements of the bands and lines listed. The wavelengths of band crests and lines were fixed from spectral data recorded photographically with a prism spectrograph. The remaining spectral data are based on the several elements which were recorded with a high-sensitivity grating flame spectrophotometer. Operating conditions used in recording the spectra with the spectrograph and

also with the flame spectrophotometer are given. Based on the spectra and spectral data presented, deductions can be made relative to the applicability and limitations of flame photometry in the determination of Sc, Y and rare-earth elements in mixtures thereof. Lanthanum, Y and Nd can be determined without spectral interference by other elements of the group studied. For all other elements of the group, some spectral interference is encountered. Nevertheless, by judicious selection of wavelength, certain of the elements may be determined flame-photometrically in the presence of many of the other elements of the group without serious interference. Two examples are cited.

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1431. **Anion effect in the flame-photometric determination of the rare-earth elements.** N. S. Poluéktov and L. A. Ovchar (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1960, **26** (8), 964–966.—The nature of the difficultly volatile compounds formed in the acetylene - air flame is studied. With soln. containing NO_3^- these are oxides, *e.g.*, Y_2O. With soln. containing SO_4^{2-}, Er and Y give $M(SO_4)_3$, and Eu and Yb give MSO_4, where M is the metal. With soln. containing PO_4^{3-}, Eu, Yb and Y give MPO_4.

G. S. SMITH

1432. **Determination of lanthanum, cerium, praseodymium and neodymium as major components by X-ray emission spectroscopy.** D. R. Maneval and H. L. Lovell (Dept. of Mineral Preparation, Pennsylvania State Univ., Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1289–1292.—Discs for the determination of La, Ce, Pr and Nd are prepared by fusion of the sample with sodium borate; standard discs are prepared similarly from the pure rare-earth oxides. This procedure is accurate, speedy and convenient, and little interference from other rare-earth oxides is encountered. The analyses of four samples of widely varying composition showed satisfactory accuracy.

K. A. PROCTOR

1433. **Successive complexometric determination of thorium and total rare-earth metals.** Yu. A. Chernikhov, R. S. Tramm and K. S. Pevzner. *Zavod. Lab.*, 1960, **26** (8), 921–924.—The soln. (25 ml), containing Th, rare-earth metals, Al, Mn, Fe, Ca, Sr, Nb and Ti, is mixed with 100 ml of water, 1 ml of 5% sulphosalicylic acid soln. and 0·5 ml of 2% ascorbic acid soln. and treated with aq. NH_3 until the pH is 1·5. After addition of 10 ml of HCl - KCl buffer soln. (pH 1·6) and 0·5 ml of xylenol orange or Alizarin red S - methylene blue soln. the cold soln. is titrated with 0·02M-EDTA to give the content of Th. The titrated soln. is then treated with aq. NH_3 until the pH is 4, 10 ml of a buffer soln. (pH 4·5) is added together with 0·5 ml of indicator soln. as before, and the boiling soln. is titrated with 0·02M-EDTA (disodium salt) to give the content of rare-earth metals plus Mn. The content of Mn is determined separately and a correction (0·09 ml of 0·02M-EDTA for each mg of Mn) is made.

G. S. SMITH

1434. **Ion-exchange separation and spectrographic determination of some rare earths in beryllium, uranium, zirconium and titanium metals, alloys and oxides. Collection with calcium and magnesium fluoride and ion-exchange separation.** S. Kallmann, H. K. Oberthin and J. O. Hibbits (Ledoux and Co., Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1278–1281.—*Procedure*—The sample (10 to 50 g) is dissolved in aq. HF and the acid concn. is raised to $\simeq$ 2·5M by the addition of more HF. Yttrium chloride carrier is added ($\equiv$ 15 mg of Y_2O_3) and a soln. of Ca and Mg (0·25 g of CaO and 0·25 g of MgO dissolved in 10 ml of 6N-HCl, evaporated to dryness and dissolved in 20 ml of H_2O). The mixed fluorides are pptd. by heating for 1 hr. on a steam bath and setting aside for 3 hr. The ppt. is filtered off, ignited, converted into sulphate, and dissolved in N-HCl; any residual Be, U, Ca and Mg are separated from the rare-earth metals on a cation-exchange or mixed cation - anion exchange column. The Y and rare-earth metals are eluted with 12N-HCl, pptd. as oxalates, ignited to oxides and weighed, and the ratio of rare-earth metals to Y is determined spectrographically. From the known added weight of Y_2O_3 and the total yield of mixed oxides the original rare-earth-metal content of the sample can be calculated.

T. R. ANDREW

1435. **Investigation of the spectrographic analysis of high-purity rare-earth oxides.** Yoshio Garrick Ishida (Kentucky Univ., Lexington, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. ORO-279, 1959. 79 pp.—An investigation of the spectrographic analysis of high-purity rare earths containing trace amounts of other rare earths was made. The study was conducted in a controlled atmosphere of O - Ar (1:4), with d.c. arc excitation. Working curves and limits of detection were determined for Dy, Gd and Tb in an yttrium matrix; for Er, Lu and Tm in an ytterbium matrix; for Dy, Er and Y in a holmium matrix; and for Pr, Sm and Eu in a neodymium matrix. The minimum detectabilities of Y, Tb and Ho were found in a dysprosium matrix. The concn. of the impurities covered in the working curves ranged from 0·005 to 2·00%. The average precision of the determinations was < 8%. The order of volatility of the rare-earth oxides in the O- Ar atmosphere was observed. The volatility was found to increase as the heats of vaporisation of the rare-earth metals decreased. Neodymium was the only rare-earth metal studied that showed a discrepancy in the correlation between volatility and heat of vaporisation. Working curves and limits of detection were determined for Dy and Ho employing a copper electrode - interrupted discharge method. Concn. from 1 μg to 60 μg per ml of the rare-earth oxides were used in the construction of the working curves. The average precision was < 5% for the working curves. A proposed method of calculating concn. ratios was tested and gave good accuracy in determining the relative amounts of Dy and Ho present in a series of samples. The sensitivities of the controlled atmosphere - d.c. arc and copper electrode - interrupted discharge method were compared. The sensitivity in detecting absolute amounts of rare-earth metals was of the same magnitude for the two methods. In terms of relative amounts, the sensitivity of detection of the d.c. arc method was superior to that of the copper electrode method.

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1436. **Photometric determination of cerium by means of o-tolidine.** N. Iordanov and K. Daiev (Sofia Univ., Bulgaria). *Zhur. Anal. Khim.*, 1960, **15** (4), 443–445.—*o*-Tolidine (**I**) is a selective and sensitive reagent for the determination of Ce. Add $La(NO_3)_3$ soln. as collector (1 ml) (12 mg per 10 to 200 μg of Ce) to the sample soln., dilute to

7 to 8 ml, precipitate La plus Ce with an equal vol. of satd. cold oxalic acid soln., and set the mixture aside till the next day. Then filter off, dry, and ignite the ppt. at 800° to 900°. Dissolve the residue in hot conc. H_2SO_4 (10 to 12 drops) and to the anhyd. yellow $Ce(SO_4)_2$ obtained add 0·05% **I** soln. in 10% H_2SO_4 (1 ml). Dilute the soln. to 100 ml and measure the extinction at 410 mμ. Beer's law is obeyed for conc. up to 3 μg of Ce per ml. The mol. extinction coeff. is ≃ 9500. The reaction with **I** is 20 times as sensitive as that with H_2O_2, and the determination is possible in the presence of Th, rare-earth metals and large amounts of Fe, Al, Mn and Ti. The method can be modified for the determination of Ce in apatite, titanite and monzonite. K. R. Cook

1437. **Spectrographic determination of yttrium in coal ash.** N. V. Arnautov and L. D. Shipilov. *Geologiya i Geofizika*, 1960, (1), 115–117; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,066.—*Procedure*—Mix the sample with powdered carbon (1:1) and place in a cavity (diam. 3 mm, depth 3·5 mm, wall thickness 0·7 mm) in a carbon electrode. Excite the spectra in an a.c. arc at 9 amp. with a carbon upper electrode, and photograph in a medium Hilger spectrograph with a slit-width of 0·015 mm. Construct a calibration curve of log (I_Y/I_b) *vs.* log C (b = background) from the line 3327·87 A in the concn. range 0·001 to 0·4%. The reproducibility is within 10%. Prepare standards by adding Y_2O_3 to the ash. The concn. of Y in ash ranges from 0·002 to 0·02%. C. D. Kopkin

1438. **Rapid analysis of erbium by neutron activation followed by gamma-ray spectrometry.** Minoru Okada (Gov. Chem. Ind. Res. Inst., Tokyo). *Nature*, 1960, **188**, 52.—Place the sample (1 to 1000 mg), sealed in a polyethylene capsule, for 3 sec. in a neutron flux of 4×10^{10} per sq. cm per sec., cool for 5 sec., count for 3 sec., cool again for 2 sec. and count for 3 sec. Measure the pulse height of the peak due to the 0·208-MeV γ-radiation of ^{167m}Er. The coeff. of variation, estimated by the use of 7 standard samples, is ≃ 10%. Most of the variation seems to originate from error in time measurement. A. R. Rogers

1439. **Coulometric determination of europium and ytterbium at controlled potential.** E. N. Wise and E. J. Cokal (Chem. Dept., Univ., Tucson, Arizona, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1417–1419.—Both Eu^{III} and Yb^{III} are reduced with nearly 100% current efficiency in 0·1M-tetraethylammonium bromide in methanol. The $E_{\frac{1}{2}}$ = 0·0 and − 0·78 V *vs.* the methanolic silver - silver bromide electrode. In samples containing both Eu and Yb, the sum only can be determined at − 1·2 V. The Eu is then determined by the method of Shults (*Ibid.*, 1959, **31**, 1095) and Yb is found by difference. The accuracy for 0·5 to 20 micro-equiv. is within 0·05 micro-equiv., but Nd and, to a less extent Sm, interfere with the determination of Yb. J. P. Stern

1440. **Determination of carbon on non-conducting catalysts by induction heating - conductimetric method.** R. J. Fox, J. W. Robinson and E. W. Seefield (Esso Res. Lab., Div. of Humble Oil and Refining Co., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 328–332 (in English).—The sample, containing ≃ 0·2 mg of C, is mixed with tin powder and iron chips and heated in a commercial h.f. induction furnace (Lindberg LI–501F). The CO_2 evolved is absorbed in $Ba(OH)_2$ soln. in a commercial conductimetric carbon-determination apparatus (Leco 515). The standard deviation is stated to be ± 0·007 at the 0·07% level of C (15 determinations). T. R. Andrew

1441. **Displacement technique for the contaminant-free precipitation of carbon dioxide as barium carbonate.** J. Goodman and J. Steigman (Polytech. Inst., Brooklyn, N.Y., U.S.A.). *Chemist Analyst*, 1960, **49** (3), 86.—The apparatus permits the pptn. of CO_2 as $BaCO_3$ without clogging of the bubbler, or exposure to the atmosphere. It is readily constructed from a 150-ml conical flask, two ground glass joints and a medium-porosity filter-crucible. P. D. Parr-Richard

1442. **Determination of carbon disulphide in the reaction mixture for the synthesis of xanthate.** E. M. Idel'son. *Zavod. Lab.*, 1960, **26** (8), 947–948.—The CS_2 is extracted from the reaction mixture with benzene and the extract is treated with alcoholic KOH soln. The xanthate that is formed is extracted with water, the soln. is treated with acetic acid, and the neutral soln. is titrated with 0·05N-iodine in the presence of starch. Alternatively, the benzene extract is treated with diethylamine and the colour is compared with that of standards. G. S. Smith

1443. **Detection of carbonyl sulphide.** H. Gamsjäger (Montanist. Hochsch., Leoben, Austria). *Mikrochim. Acta*, 1960, (5–6), 758–761 (in German).—The catalysis of the iodine - azide reaction is used for the detection of COS. The limit of detection is between 25 and 50 μg. The COS may be concentrated either by absorption in ethanolic KOH and regeneration by acidification, when the sensitivity is increased to 5 μg, or in acid $PdCl_2$ soln., when PdS is formed; COS may be detected in 99·6% pure CO_2. Other sulphides, especially H_2S and CS_2, interfere. J. P. Stern

1444. **Photometric determination of silicon as γ-molybdosilicic acid.** W. Kemula and S. Rosolowski (Dept. Inorg. Chem., Univ., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 419–428.—On boiling the acid soln. (pH 0 to 4) of α- and β-molybdosilicic acids for 30 min., a γ-molybdosilicic acid is formed, to which the formula $H_4[Si(Mo_2O_{10})_4].nH_2O$ is ascribed. As this form is more stable (instability constant = $2·0 \times 10^{-14}$) it is more suitable for the colorimetric determination of silicon as the yellow complex at 420 mμ, since critical time and pH effects are eliminated; it is also suitable for the determination of Si in the presence of phosphates, since it is not affected by the large excess of citric acid used to decompose the molybdophosphate complex. P. Brych

1445. **Trace analysis of high-purity silicon.** F. A. Pohl and W. Bonsels (A.E.G. Res. Inst., Frankfurt-Main). *Mikrochim. Acta*, 1960, (5–6), 641–649 (in German).—Traces down to 1 p.p.m. of Pb, Cd, Fe, In, Cu, Ni, Tl, Bi and Zn in semi-conductor silicon are determined polarographically in a Southern Instruments K 1000 polarograph with errors ≯ 20%. Factors influencing accuracy and sensitivity include the method of pulverisation, the avoidance of inorganic reagents and working in a closed system. A micro-cell of 0·2-ml capacity is illustrated. *Procedure*—Dissolve the sample (1 g) at 100° in 40% HF (15 ml, added dropwise), in presence

of $HClO_4$ (0·5 ml) and HNO_3 (5 ml), and remove the acids and SiF_4 at 150°. Oxidise the dry residue with 30% H_2O_2 and extract the Fe and Tl into isopropyl ether (3 × 1 ml). Remove organic matter from both phases by evaporation and treatment with H_2SO_4 (1 drop) and $HClO_4$ (0·2 ml) at 200°. Dissolve the residue of the acid phase in 6N-aq. NH_3 (0·2 ml) and polarograph in an atmosphere of H, determining Cu at − 0·42 V, Cd at − 0·70 V, Ni at − 0·98 V and Zn at − 1·27 V; dissolve the acid residue from a parallel run in 0·5M-Na tartrate (0·2 ml) at pH 4·5 and determine Bi at − 0·49 V, Pb at − 0·71 V, In at − 0·82 V and Zn at − 1·49 V. Warm the residue from the organic phase with 6N-H_2SO_4 (3 drops) and 1% aq. hydrazine sulphate (1 drop), evaporate to dryness, and dissolve the residue in 0·5M-ammonium tartrate in N-aq. NH_3 (0·2 ml); determine Tl at − 0·36 V and Fe at − 1·39 V. J. P. STERN

1446. **Quantitative spectrochemical analysis of minor elements in silicates with double internal standards.** H. Hamaguchi, R. Kuroda and R. Negishi (Chem. Dept., Univ. of Education, Koishikawa, Tokyo). *Bull. Chem. Soc. Japan*, 1960, **33** (7), 901–905.—The use of Sb_2O_3 (**I**) and palladium black (**II**) as internal standards for volatile and non-volatile elements, respectively, in the spectrographic analysis of silicates, is described. **I** was used for determining Ga, Pb and Sn, and **II** for Ni, Co, Cr, V and Sc. **I** and **II** were mixed with carbon powder as buffer to give concn. of 0·8% (for **I**) and 0·04% (for **II**). Selected internal standards and analysis lines, with their excitation potentials and analysis ranges, are listed. E. M. MAYES

1447. **Spectrographic determination of germanium and gallium in coal.** A. N. Bronshtein, T. I. Sendul'skaya and M. Ya. Shpirt (Inst. of Mineral Fuels, Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (8), 973–974.—The finely divided material is ashed with free access of air at 600° and mixed with an equal wt. of a buffer mixture containing carbon powder and NaCl (1 : 1) with 0·1% of SnO_2 to provide an internal standard. The spectrum of the mixture (20 mg) in a carbon electrode is excited by means of an a.c. arc (8 amp.), and the lines Ge 2651·18, Ga 2943·64, Sn 3034·12 and Sn 2839·99 A are measured. The method is suitable for contents between 0·001 and 1%. In the presence of > 0·1% of Ge or Ga the sample is diluted with SiO_2. G. S. SMITH

1448. **Determination of small amounts of aluminium in tin.** M. I. Shvaĭger and É. I. Rudenko (Magnitogorsk Metallurgical Combine). *Zavod. Lab.*, 1960, **26** (8), 939.—The sample (1 g) is dissolved in aqua regia and the soln. is evaporated several times with additions of HCl to remove Sn as $SnCl_4$. The residue is treated with 1 to 2 ml of H_2SO_4 (1 : 1), the soln. is evaporated, 2 ml of HCl (1 : 10) is added, and the soln. is again evaporated. The residue is dissolved in 2 ml of HCl (1 : 10), 0·85 ml of 10% NaOH soln. is added, and the soln. is diluted to 25 ml. An aliquot (2·5 ml) is treated with 0·2 ml of 5% ascorbic acid soln., 0·3 ml of 0·3% Chrome azurol S (C.I. Mordant Blue 29) (*cf.* Kashkovskaya and Mustafin, *Ibid.*, 1958, **24**, 1189) and 7 ml of an acetate buffer soln. (pH 5·37). After 5 min. the extinction is measured with a green filter. G. S. SMITH

1449. **The use of dithizone as internal indicator in precipitation titrimetry. II. Direct volumetric determination of lead as lead phosphate.** M. Vancea and M. Voluşniuc (Inst. Chem., Acad. R.P.R., Cluj, Romania). *Stud. Cercet. Chim., Cluj.*, 1959, **10** (2), 275–278.—Lead acetate soln. (≃ 0·1N) (10 to 20 ml) is added to acetic acid - Na acetate buffer (pH 4·5) (5 to 10 ml) and 1 ml of dithizone soln. in $CHCl_3$. The soln. is titrated with 0·1N-KH_2PO_4 until the brick-red colour changes to green. N. E.

1450. **Determination of traces of lead in prehistoric alloys. The use of a corundum rod as a scraping and crushing device.** H. Ballczo (Anorg. u. Phys. Chem. Inst., Univ. Wien, Austria). *Mikrochim. Acta*, 1960, (5–6), 973–982 (in German).—A small corundum rod is used to scrape off a 2-mg sample with minimum damage to the test-piece. The sample is dissolved in HNO_3 and evaporated almost to dryness; a second evaporation precipitates metastannic acid. After neutralisation with NH_3 vapour, the salts are dissolved in Ni - EDTA soln. and transferred to paper impregnated with Na_2SO_4. After treatment of the paper with tartrate buffer (pH 2·8), $PbSO_4$ is detected with Na rhodizonate. Large amounts of Cu and Sn do not interfere. P. D. PARR-RICHARD

1451. **Apparatus for the automatic determination of lead in ores and concentrates.** A. A. Khaĭdarov and A. P. Novikov. U.S.S.R. Pat. 127,473 (25th March, 1960).—The apparatus is designed for measurement with photo-electric multipliers, by the compensation method, of the bremsstrahlung γ-radiation caused by the lead in the sample and a standard when both are simultaneously irradiated with β-rays. The apparatus has a cathode follower with an intermediate amplifier in each arm of the bridge circuit. C. D. KOPKIN

1452. **Determination of lead and tin in lead - tin solder alloys by controlled-potential electrolysis.** B. Alfonsi (Fiat Lab., Turin, Italy). *Anal. Chim. Acta*, 1960, **23** (4), 375–380 (in English).—Dissolve the sample (1 g) in 2 g of $K_2S_2O_7$ and 15 ml of H_2SO_4, cool, add HCl (1 : 3) (25 ml), $KMnO_4$ soln. (5%) (10 to 12 drops), tartaric acid (8 g in 25 ml) and aq. NH_3 until the soln. is clear (pH 6 to 8·5). Add succinic acid (2 g) and, slowly, hydrazine dihydrochloride (1 g). Adjust the pH to 7·2 to 7·3 or, if necessary to keep $PbSO_4$ in soln., to the value needed to produce a clear soln. (≯ 8·5). Deposit Pb (with some Cu, Bi and Ag) on a copper-plated platinum electrode at a potential of − 0·65 V *vs.* the S.C.E. until the current falls to ≃ 0·05 amp., when the pH should be adjusted to 5 and electrolysis continued till the current falls to 0·01 amp. After removal of the lead-plated electrode, add HCl (30 ml) and hydrazine dihydrochloride (0·2 g) to the soln. and electrolyse at ≯ 1 amp., and finally at − 0·65 V *vs.* the S.C.E. The determination of both Pb and Sn may be completed in less than 3 hr. Results for Pb (0·1 to 0·8 g) are within ± 1 mg and for Sn (0·1 to 0·8 g) are within ± 0·5 mg of the amounts added. T. R. ANDREW

1453. **Flame-spectrophotometric determination of calcium in lead metal.** R. E. Barringer (Union Carbide Nuclear Co., Y–12 Plant, Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. Y–1295, 1960. 19 pp.—A flame-spectrophotometric method for the determination of Ca in lead metal in the range of 0·02 to 0·1% was developed. A minimum of sample preparation and time is

required. Measurement of the Ca emission at 554 mμ gave limits of error (p = 0·95) of ± 4·2%.
NUCL. SCI. ABSTR.

1454. **Arsenate method for the iodimetric determination of titanium in the presence of other cations.** G. B. Shakhtakhtinskiĭ and A. M. Mukimov. *Azerbaidzh. Khim. Zhur.*, 1959, (3), 59–63; *Ref. Zhur., Khim.*, 1960, (15), Abstr. No. 61,054.—Precipitate Ti^{4+} from an acetic acid medium containing 1% of free H_2SO_4 with Na_3AsO_4; Ag^+, Hg^{2+}, Cu^{2+} and Cd^{2+} do not interfere. Dissolve the ppt. in H_2SO_4 and titrate the liberated H_3AsO_4 iodimetrically; Bi^{3+}, Sb^{3+}, Sn^{2+} and Sn^{4+} are co-pptd. with Ti and lead to high results. When titanium arsenate is pptd. from 3% HNO_3 soln. in the absence of H_2SO_4, much less Pb is co-pptd. than from 1% HNO_3 soln. K. R. COOK

1455. **Separation of titanium from manganese by the ion-exchange method.** I. K. Tsitovich (Kuban Agric. Inst., Krasnodar). *Zhur. Anal. Khim.*, 1960, **15** (4), 503–504.—The distribution coeff. of $[TiO(H_2O_2)]^{2+}$ and MnO_4^- between the cationites KU-1, KU-2 and SBS and HCl soln. (0·1 to 10N) were studied and results are tabulated. To separate Ti from Mn when they are in the ratios of 1:1000 to 1000:1 use a column (height 10 cm, diameter 1 cm) filled with cationite KU-1 (H^+ form). Wash it with 0·5N-HCl, pour in the test soln. (0·5N with respect to HCl), elute Mn with 0·5N-HCl at the rate of 30 drops per min., and elute Ti with 4N-HCl. Titanium forms anion complexes in > 8N HCl soln. K. R. COOK

1456. **Photometric determination of zirconium as the molybdophospho-zirconium complex.** R. M. Veĭtsman (All-Union Sci. Res. Inst. of Hard Alloys). *Zavod. Lab.*, 1960, **26** (8), 927–929.—The acid (H_2SO_4) soln. (20 ml) containing from 1 to 25 mg of Zr is mixed with 10 ml of 10% K citrate soln., then neutralised to Congo red paper with aq. NH_3, and diluted to 200 ml. An aliquot (20 ml) is treated with 20 ml of water, 0·5 ml of 5% $(NH_4)_2HPO_4$ soln. and 3 ml of 10% $(NH_4)_2MoO_4$ soln. and then neutralised with H_2SO_4 (1:4), with Congo red paper as indicator. The soln. is diluted to 100 ml and set aside for 10 to 15 min. An aliquot (20 ml) of the yellow soln. is treated with 15 ml of 4% EDTA (disodium salt) soln. The time is noted and 10 ml of H_2SO_4 (1:4) is added at once, followed after 30 sec. by 1 ml of 0·1% $SnCl_2$ soln. After being mixed for 2 to 5 sec. the soln. is diluted to 100 ml, and the extinction is measured with a red filter. The content is calculated by means of a calibration curve.
G. S. SMITH

1457. **Radiochemical separation of zirconium-95 and niobium-95 with tri-n-butylphosphine oxide.** Hirokazu Umezawa and Reinosuke Hara (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Anal. Chim. Acta*, 1960, **23** (3), 267–270 (in English). —A separation scheme is presented for ^{95}Zr and its daughter ^{95}Nb, based on the extraction of the ^{95}Zr into 0·005M-tri-n-butylphosphine oxide in CCl_4 from 2N-HNO_3. The ^{95}Nb remains in the aq. phase. The recovery of ^{95}Zr is 95%. Separation from HCl soln. was not possible. H. M.

1458. **Rapid chromatographic semi-quantitative micro-determination of total zirconium and hafnium in sulphuric and oxalic acid media.** A. Górski and J. Moszczyńska (Dept. of Metallurgy, Inst. of Technol., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (3), 395–400.—The method is suitable as a production control test, and can be used for detecting 6 μg of Zr plus Hf in 1 ml of the strongly acid eluates from ion-exchange columns. The chromatograms are prepared on columns (100 mm × 4 mm) packed with acid-washed alumina by the dropwise addition of 0·1 ml of 0·15% Alizarin red S soln. followed by 0·1 ml of the sample. The intensity and position of the brown rings given by the metal - dye complexes depends on the concn. of the metals, and a semi-quant. estimation is obtained by comparison with freshly prepared standards or a permanent colour chart.
P. BRYCH

1459. **Spectrophotometric determination of zirconium in magnesium-base alloy.** Shozo Shibata, Yoshio Ishiguro and Teiichi Matsumae (Gov. Ind. Res. Inst., Nagoya, Japan). *Anal. Chim. Acta*, 1960, **23** (4), 384–387 (in English).—Arsenazo reacts with Zr in acid soln. (pH 1·6 to 2·0) to give a blue colour (max. absorption at 578 mμ), which obeys Beer's law up to at least 20 p.p.m. of Zr (extinction ≃ 0·5 at 578 mμ in a 1-cm cell). Aluminium, Mg, Cu, Fe, Ce, Ti, U, acetate, SO_4^{2-}, Cl^- and NO_3^- do not interfere; Th, Nb, Ta, citrate, oxalate, tartrate, PO_4^{3-} and ClO_4^- must be absent. The technique has been applied to the determination of Zr (0·01 to 1%) in magnesium alloys.
T. R. ANDREW

1460. **Colorimetric determination of hafnium oxide in admixture with zirconium oxide.** L. I. Kononenko, R. S. Lauer and N. S. Poluéktov. *Ukr. Khim. Zhur.*, 1959, **25** (5), 633–638; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,061.—The coloured complexes of Zr and Hf with arsenazo (**I**) behave differently as the HCl concn. of the soln. is increased, the complex of Hf being decolorised to a greater extent than that of Zr. In N-HCl, the extinction of a soln. of the Hf complex is one-nineteenth, and that of the Zr complex one-half, that in 0·25N-HCl, so that by measuring the extinctions of a soln. of the complex with **I** at 0·25N and at 1·0N with respect to HCl, the content of Hf in a mixture with Zr can be determined. The different behaviour with respect to increasing HCl concn. may be due to the different degrees of dissociation of the Zr and Hf complexes, the apparent dissociation constants of which are $0·12 \times 10^{-10}$ and $0·86 \times 10^{-10}$, respectively. *Procedure*—Dissolve 15 mg of the sample of mixed HfO_2 and ZrO_2 in 2 to 3 ml of HF, evaporate the soln. with 2 ml of conc. $HClO_4$ and 10 ml of a 4% H_3BO_3 soln. (to remove F^-), dissolve the residue in N-HCl and make up to 250 ml with N-HCl. Take two 5-ml aliquots of the soln., add to each 30 ml of water, to the first add 1·88 ml and to the second add 11·25 ml of 4N-HCl; add to each soln. 2·5 ml of 1% gelatin soln. and 5 ml of 0·1% **I** soln., make up to 50 ml and measure the extinctions at 570 mμ in 1-cm cells against a reagent blank. Calculate the ratio of the extinctions in 0·25N- and 1·0N-HCl and obtain the HfO_2 content from a calibration curve. The method can be used to determine from 20% upwards of HfO_2 in mixtures of HfO_2 and ZrO_2 with an abs. error ranging from − 4·0 to + 6·0%. C. D. KOPKIN

1461. **Arsenate method for the iodimetric determination of thorium.** G. B. Shakhtakhtinskiĭ and I. A Mamedov. *Azerbaidzh. Khim. Zhur.*, 1959, (2), 105–110; *Ref. Zhur., Khim.*, 1960, (15), Abstr. No. 61,059.—*Proceedure*—Heat the test soln. (15 ml

to boiling, and add a slight excess of aq. NH_3 soln. (1:5). Add boiling 0·5N-Na_3AsO_4 (15 ml) neutralised to methyl red and boil the soln. and ppt. ($ThOHAsO_4$) for ≃ 10 min. Filter through a sintered-glass crucible (No. 4), wash the ppt. (× 7) with hot H_2O and dissolve it in H_2SO_4 (2:5) (25 to 30 ml). Add benzene (20 to 25 ml) and 2N-KI (3 ml), stir for a few seconds, dilute the aq. layer with an equal vol. of H_2O and titrate with $Na_2S_2O_3$ soln. until the benzene layer is colourless; 1 ml of 0·1N-$Na_2S_2O_3$ ≡ 0·0116 g of Th.

K. R. Cook

1462. **Estimation and separation of thorium with dihydroxytartaric acid.** G. R. Amladi and Y. V. Lawande (St. Xavier's Coll., Bombay). *J. Univ. Bombay*, 1960, **27**, 24–28.—Thorium nitrate is quant. pptd. from acid soln. with 2% dihydroxytartaric acid soln. (**I**) above pH 0·6; La and Ce are also pptd. by **I**, but from less acid soln. Thorium in mixtures with lanthanum and cerium nitrates (1:4:4) is separated by adjusting the pH to 0·7 to 1·0, treating with **I** to precipitate Th, re-dissolving in conc. HNO_3, evaporating, extracting with water, re-adjusting the pH to 0·7 to 1·0, and re-pptg. with **I**. **I** gives as good results in the extraction of Th from monazite sands as one of the usual reagents, *e.g.*, *m*-nitrobenzoic acid.

Chem. Abstr.

1463. **Thorium determinations with 8-hydroxyquinaldine.** A. Corsini and R. P. Graham (Burke Chem. Lab., McMaster Univ., Hamilton, Canada). *Anal. Chim. Acta*, 1960, **23** (3), 248–256.—The determination of Th with 8-hydroxyquinaldine (**I**) has been studied and the essential conditions have been established. (*i*) A 70% excess of **I** must be present if the ppt. is to be only the 1:4 chelate. For concn. of Th < 0·7 mg per ml the excess should be as for 0·7 mg per ml; this can be achieved by using a fixed amount of **I** and keeping the Th concn. below 0·7 mg per ml. (*ii*) The pH must lie between 6·1 and 11·5, and the manner of adding the aq. NH_3 used to give this pH is important. The concn. of aq. NH_3 must not exceed 1·0M and it must be added dropwise with very vigorous stirring. If this is not done the ppt. will consist partly of hydrated ThO_2. (*iii*) The ppt. should be digested at 70° for ≮ 1 hr., in order to convert any small amounts of hydrated ThO_2 into the chelate. The final determination of Th can be carried out bromimetrically, or gravimetrically by drying the ppt. for 1 hr. at 110° and weighing it as $Th(C_{10}H_8ON)_4$.

H. M.

1464. **Derivatives of 1,4-dihydroxyanthraquinone as metal indicators in the titration of thorium with disodium EDTA.** E. G. Owens, II, and J. H. Yoe (Pratt Trace Analysis Lab., Univ. of Virginia, Charlottesville, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 321–324 (in English).—2-Phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) (**I**) and quinizarin-2-sulphonic acid (sodium salt) (**II**) are advocated as having advantages over Alizarin red S (**III**) in the complexometric titration of Th. Suitable pH ranges for these indicators are—1·4 to 3·4 for **I**; 2·0 to 3·4 for **II**; and 2·2 to 3·4 for **III**. The colour changes at the end-point are sharpest with **I**.

T. R. Andrew

1465. **A re-investigation of the determination of thorium with SPADNS [sodium 4,5-dihydroxy-3-(4-sulphophenylazo)naphthalene-2,7-disulphonate].** J. A. Cooper and M. J. Vernon (Dept. of Geophysics, Australian Nat. Univ., Canberra). *Anal. Chim. Acta*, 1960, **23** (4), 351–354 (in English).—Attempts to repeat the work of Banerjee (*Anal. Abstr.*, 1957, **4**, 2156) have proved unsuccessful, an extinction of 0·4 for 100 µg of Th per 25 ml being found as compared with the previously reported value of 0·4 for 4 µg of Th. The sensitivity is given as 0·011 µg of Th per sq. cm for log I_0/I = 0·001 at 580 mµ, while Banerjee quoted 0·012 µg of Th per sq. cm, indicating a discrepancy in the earlier work. The effects of reagent concn. and acetate buffer concn. are reported.

T. R. Andrew

1466. **Rapid determination of thorium by fluoride titration using some chromotropic [acid] azo dyes.** S. K. Datta [Victoria (Govt.) College, Coochbehar, India]. *Bull. Chem. Soc. Japan*, 1960, **33** (7), 882–884.—The titrimetric determination at pH 2·4 to 2·8 of up to 50 mg of Th per 50 ml of soln. with NaF, with 0·5 ml of 0·1% nitroso-SNADNS-4, SNADNS-6 and CHPADNS, is described. These dyes, which are prepared from 4-aminonaphthalene-1-sulphonic acid, 5-aminonaphthalene-2-sulphonic acid and 4-aminosalicylic acid, respectively, form pink to violet complexes with Th, which are decomposed by fluoride with a marked colour change. Interfering substances include iron, cerium, rare-earth metals and alkaline-earth metals, phosphates, borates, oxalates, tartrates and citrates.

E. M. Mayes

1467. **Photometric determination of thorium in minerals with arsenazo II.** S. B. Savvin, M. P. Volynets, Yu. A. Balashov and V. V. Bagreev (Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 446–451.—The method is suitable for the determination of 10^{-2} to 10^{-4} % of Th in minerals. Two methods are recommended for the isolation of Th, namely, double fluoride pptn. and fluoride-oxalate pptn.

K. R. Cook

1468. **Analytical chemistry of thorium. II. Complexometric determination of thorium in monazite concentrates after its isolation on KU-2 cationite.** Yu. A. Chernikhov, V. F. Luk'yanov and A. B. Kozlova. *Zhur. Anal. Khim.*, 1960, **15** (4), 452–454.—*Procedure*—Fuse the monazite concentrate (2 g) with Na_2O_2 (10 to 12 g) at 600° to 650°, leach the melt with hot H_2O, filter off the residue and wash it with 5% NaOH soln., followed by hot HCl (1:1). Evaporate the soln. almost to dryness, add conc. HCl (20 ml) and H_2O (20 ml) and filter off the residue containing $ZrO_2(P_2O_5)_4$. Add 20% tartaric or trihydroxyglutaric acid soln. (5 ml) to the combined filtrate and washings and dilute to 100 ml. Pass a 25-ml aliquot of the soln. through a column (height 24 cm, diam. 1·5 cm) containing iron-free KU-2 resin (grain size 0·16 to 0·3 mm) (20 to 25 ml). Wash the column with 10 to 15-ml portions of 20% HCl (70 ml); the final percolate should be colourless. Then pass 20% NH_4Cl soln. (50 ml) through the column, and finally elute Th with 5 to 7-ml portions of 20% ammonium carbonate soln. (50 ml). Wash the column with H_2O (20 to 30 ml) and add the washings to the eluate. Add HCl (1:1) to the combined soln. to decompose the ammonium carbonate, then boil the soln. for 2 to 3 min. Adjust the pH of the soln. with aq. NH_3 soln. to 2·4 to 2·6 (to 2,4-dinitrophenol), add 0·5% aq. xylenol orange soln., and titrate with ≃ 0·2M-EDTA to a lemon-yellow end-point. Good recoveries (tabulated) are obtained by this method.

K. R. Cook

1469. **Radiometric determination of thorium in tungsten and molybdenum.** L. N. Aleksandrov. *Zavod. Lab.*, 1960, **26** (8), 975–977.—A method based on measurement of the α-radiation intensity of ^{232}Th is described. G. S. SMITH

1470. **Differential electrolytic potentiometry. IV. Application to micro-coulometric titrimetry. The determination of hydrazine at microgram levels.** E. Bishop (Univ., Exeter, England). *Mikrochim. Acta*, 1960, (5–6), 803–815.—Hydrazine is titrated with electrically generated bromine in a microtitration apparatus (illustrated). The accuracy for 1 to 3 μg of hydrazine with a generating current of 100 μA is within ± 0·3%, and on 0·2 and 0·02 μg with a current of 10 μA it is within ± 1% and ± 5%, respectively. J. P. STERN

1471. **Colorimetric method for the estimation of azide ions.** P. J. Staples (University Coll., London, England). *Chem. & Ind.*, 1960, (39), 1210–1211.—The amount present in 5 ml of a 10^{-3} to 10^{-4}M-soln. is determined by using the reaction between N_3^- and NO_2^-. This reaction is rapid in acid and especially in acetic acid - acetate buffer soln. Sulphanilic acid is then diazotised with the excess of NO_2^-, and the diazonium salt is coupled with 1-naphthylamine to form a water-soluble stable orange - yellow dye, the extinction of which is measured at 475 mμ. Results are referred to a calibration curve. The error is 1%. When coordinated azido-groups are present they interfere by reacting with NO_2^-. The determination can then be made on the percolate after passage of the sample soln. through an ion-exchange column of IR-120 (Na^+ form). It is also possible to titrate N_3^- ($\nless 10^{-2}$M) potentiometrically with standard $AgNO_3$ soln. R. M. S. HALL

1472. **Analytical uses of bromine chloride. Determination of hydroxylamine.** K. Burger, F. Gaizer and E. Schulek (L. Eötvös Univ., Budapest, Hungary). *Talanta*, 1960, **5** (2), 97–101 (in English).—Hydroxylamine is determined by oxidation with BrCl produced by the action of HCl on a soln. containing equivalent amounts of $KBrO_3$ and KBr. *Procedure*—To the sample soln. (containing 3 to 12 mg of hydroxyammonium chloride) add sufficient 0·1N-$KBrO_3$ (2·7835 g of $KBrO_3$ and 3·9670 g of KBr per litre) to give $\nless$ 100% excess of BrCl on acidification. Dilute to 40 ml with water, add 20% HCl (5 to 10 ml) and set aside for 5 min. Add 5% KI soln. (10 ml) and titrate with 0·1N-$Na_2S_2O_3$. The error of the method is ± 0·5%. It is shown that in the method of Kurtenacker and Wagner (*Z. anorg. Chem.*, 1922, **120**, 261) the effective oxidant is a mixture of BrCl and Cl. W. T. CARTER

1473. **Determination of ammonia in the presence of volatile amines.** N. Bellen and Z. Bellen (Anal. Dept., Inst. of Gen. Chem., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 461–469.—The sample soln. (containing NH_3 equiv. to 0·1 to 0·35 g of NH_4Cl) is digested for 30 min. with sodium cobaltinitrite (25 g) and $NaNO_3$ (25 g) in acetate buffer (pH 4·8) (100 ml). The pptd. sodium ammonium cobaltinitrite is filtered off, washed with acetate buffer satd. with sodium ammonium cobaltniitrite (5 × 5 ml), and decomposed with NaOH. The liberated NH_3 is distilled with 0·2N-HCl, the excess of which is titrated with 0·2N-NaOH. The accuracy is ± 1%. This method can be used in the presence of a tenfold excess of amines. P. BRYCH

1474. **Titrimetric determination of combined carbon dioxide in anhydrous ammonia.** A. R. Adam, R. Syputa and W. E. Stephenson (Western Operations Inc., Standard Oil Co. of California, Richmond, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1319–1320.—The sample (≃ 500 ml) contained in a stainless-steel cylinder is allowed to evaporate spontaneously at a temp. maintained at < 70° F. Combined CO_2 remains in the cylinder as ammonium carbamate. The ammonium carbamate is decomposed in the cylinder with 2N-H_2SO_4 and the evolved CO_2 is carried by a stream of N through a scrubber containing 2N-H_2SO_4 and absorbed in an excess of standard $Ba(OH)_2$ soln., which is then back-titrated with oxalic acid soln. Results on synthetic mixtures containing 5 to 50 p.p.m. of CO_2 show deviations from the amounts added of $\ngtr$ 3 p.p.m. T. R. ANDREW

1475. **New method for the determination of nitrates.** P. W. West and G. L. Lyles (Coates Chem. Lab., Louisiana State Univ., Baton Rouge). *Anal. Chim. Acta*, 1960, **23** (3), 227–232.—Chromotropic acid (**I**) in conc. H_2SO_4 reacts with nitrates to give a yellow colour, the intensity of which is a measure of the nitrate concn. *Procedure*—The test soln. ($\ngtr$ 5 p.p.m. of NO_3^-) (3 ml) is added to 7 ml of reagent soln. (0·01 g of **I** in 100 ml of conc. H_2SO_4 containing 1 ml of conc. HCl) in a 10-ml flask. When the soln. has cooled to room temp. it is diluted to volume, and the extinction is read at 357 mμ and referred to a calibration graph. Oxides of N in the atmosphere may be determined by drawing the air through 7 ml of the reagent and treating as described above. Bromate, Br^-, ClO_3^-, Ti^{3+} and Ti^{4+} interfere seriously, Be^{2+}, Bi^{3+}, I^-, IO_3^-, Fe^{2+}, Fe^{3+}, MoO_4^{2-} and Ru^{3+} only slightly. Two calibration graphs must be prepared for the ranges 0·0 to 0·8 p.p.m. and 1·0 to 5·0 p.p.m. of NO_3^-, respectively. H. M.

1476. **Oxidimetric determination of small amounts of nitrate in sodium nitrite.** W. Leithe (Österr. Stickstoffwerke A.-G., Linz, Austria). *Mikrochim. Acta*, 1960, (5–6), 762–765 (in German).—After destruction of the NO_2^- with excess of hydrazine sulphate, the NO_3^- in sodium nitrite are determined by reaction with excess of 0·02N-$FeSO_4$ and back-titration with 0·01N-$K_2Cr_2O_7$. The method is used for NO_3^- contents as low as 0·05% and, for 0·2 to 1% of NO_3^-, involves errors $\ngtr$ 0·03% absolute. *Procedure*—Add the sample (1 g) in 50 ml of water to ice-cold 15% hydrazine sulphate soln. (25 ml) during 10 min. Set aside for 5 min. at room temp. and dilute to 100 ml. Add 10 ml of this NO_2^--free soln. to NaCl (2 g) and then add 0·02N-$FeSO_4$ (10 ml) and boil the soln. vigorously for 3 min. Cool the soln. and titrate the excess of $FeSO_4$ with 0·01N-$K_2Cr_2O_7$ in the presence of 0·0025M-ferroin (5 drops). Compare with a blank titrated at the same temp. J. P. STERN

1477. **Specific volumetric determination of nitrite.** H.-W. Kaloumenos (Friedrich Goetze A.-G., Burscheid bei Köln, Germany). *Werkst. u. Korrosion*, 1960, **11** (10), 626.—Sodium nitrite reacts quant. with sulphamic acid according to the equation—

$$NaNO_2 + H_2NSO_3H = NaHSO_4 + H_2O + N_2.$$

Procedure—To 20 ml of filtered test soln. add 150 ml of H_2O, 20 ml of 0·1N-sulphamic acid and 20 ml of conc. H_2SO_4. Warm the mixture to 60° ± 5° and back-titrate the excess of sulphamic acid potentiometrically with 0·1N-$NaNO_2$, at a rate

of 2 to 4 drops per sec., until the potential does not decrease on further addition of $NaNO_2$ soln. The method can be used for the analysis of pickling salt and nitrous acid derivatives in dilute and concentrated soln., and in the presence of organic solvents. R. E. E.

1478. **Optical phenomena in turbidimetric analysis applied to sulphate determination in phosphoric acid.** S.-E. Dahlgren (AB Förenade Superfosfatfabriker, Landskrona, Sweden). *Acta Chem. Scand.*, 1960, **14** (6), 1279–1287.—Optimum measuring conditions for turbidimetric analysis are discussed theoretically, but satisfactory experimental verification of the theory could not be obtained with $BaSO_4$ dispersions in 0·5% gelatin soln. Conditions recommended are that the wavelength should be $\simeq$ 410 mμ (for determinations within the range 0·05 to 0·20 mg of S per 50 ml) and that concentration and cell size should be chosen so that an extinction of 0·3 to 0·5 is obtained. A coeff. of variation of 1·5% was obtained for 12 samples under these conditions. S. M. Marsh

1479. **Titrimetric determination of phosphorus in apatite by means of ion-exchange resins.** A. Lewandowski and H. Witkowski. *Prace Kom. Mat.-Przyr. Poznań. Tow. Przyj. Nauk*, 1959, **7** (9), 3–7; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,112.—The method used is based on the complexometric titration of soluble phosphates in an ammoniacal medium, with Eriochrome black T as indicator [*cf. Ref. Zhur., Khim.*, 1956, (13), Abstr. No. 39,860]. *Procedure*—Treat 1 g of the finely ground sample with a mixture of conc. HNO_3 and HCl (1:3) and evaporate to dryness. Add 0·5 ml of conc. HCl and again evaporate to dryness, and repeat to render silicic acid completely insoluble. To the residue add 1 or 2 ml of conc. HCl, dilute, filter, and make up to 100 ml. To remove interfering elements, pass 20 ml of the soln. through a column containing 10 g of a phenolsulphonic resin (H^+ form) and wash with water to give a total volume of 100 to 120 ml; evaporate the soln. to 10 or 20 ml, add 30 ml of buffer soln. (50 g of NH_4Cl and 400 ml of conc. aq. NH_3 in 1 litre) and 2 or 3 drops of Eriochrome black T soln., add standard $MgSO_4$ soln. ($\simeq$ 0·1M), set aside for 20 min., filter off the pptd. $MgNH_4PO_4$ and titrate the excess of $MgSO_4$ with 0·1M-EDTA (disodium salt). The results agree to within $\simeq$ 1% with those by the gravimetric method. C. D. Kopkin

1480. **Rapid determination of soluble phosphoric anhydride in open-hearth slags.** N. N. Lapin and N. S. Prilutskaya. *Sb. Nauch. Trud. Zhdanovsk. Metallurg. Inst.*, 1960, (5), 387–392; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,114.—Phosphorus compounds are dissolved in citric acid with subsequent photometry as yellow molybdovanadophosphoric acid. *Procedure*—Add 5 ml of ethanol to the sample of finely ground slag (2·5 g), make up to 250 ml with 2% citric acid soln., shake mechanically for 15 min. and filter through a dry filter, discarding the first 50 ml. Make up 50 ml of the filtrate to 500 ml; to 10 ml of the soln. add 40 ml of water and 30 ml of reagent [mix equal vol. of HNO_3 (1:2), 25% NH_4VO_3 soln. and 5% ammonium molybdate soln.; set aside for 4 to 6 days before use]. Dilute to 100 ml and after 5 min. measure the extinction in a 20-mm cell with a blue filter. A single determination takes 25 min.; the relative error is $\not>$ 1·6%. The presence of SiO_2 (0·7 to 0·8 mg) does not interfere. It is shown that all P-containing compounds found in open-hearth slag are soluble in 2% citric acid soln., which enables the value of the slag to be deduced from the result. C. D. Kopkin

1481. **Quantitative determination of the composition of Graham's salt.** A. Swinarski and M. Piotrowska (Dept. of Inorg. Chem., Copernicus Univ., Toruń, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 435–443.—An investigation of the method of Jones (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 536) showed that pH values and digestion times significantly influence the results, and the following refinements are therefore proposed. The precipitation of polyphosphates with $BaCl_2$ should be carried out at pH 3·0, and the ppt. should be filtered off after digestion for 20 min. Trimetaphosphates are determined in the filtrate, and the separation of ortho- and pyro-phosphates with $BaCl_2$ should be carried out at pH 8, with digestion for 30 min. To avoid possible hydrolysis of polyphosphates, sample soln. should be prepared immediately before the analysis. These modifications were tested by analysing ten samples from each of two batches of Graham's salt, and the following mean errors (as % of sample) were obtained—total P_2O_5 0·08, 0·05; polyphosphate 0·43, 0·48; trimetaphosphate 0·51, 0·45; orthophosphate 0·65, 0·51; and pyrophosphate 0·30, 0·23. P. Brych

1482. **Detection of polyphosphates by paper chromatography.** F. Bukatsch. *Mikrokosmos*, 1959, **48**, 276–278.—The apparatus is described. Under favourable conditions satisfactory separation of the various phosphates is achieved in about 3 hr. After development the paper is sprayed with a soln. containing equal parts of 7·5% aq. ammonium molybdate soln. and conc. HNO_3. The zones of molybdophosphate thus produced are made visible by reduction to molybdenum blue in bright sunlight. With a 1-drop sample containing a concn. of 1% of each acid (sodium salt) the ultimate positions occupied on the chromatogram are as follows—near the top, where the sample was applied, hexaphosphoric acid; next in order are tetra- and tri-phosphoric acids, pyrophosphoric and orthophosphoric acid. Analysis of sausage and similar meat products can be carried out by using 1 drop of soln. obtained by extracting with glacial acetic acid or with 20% trichloroacetic acid. Chem. Abstr.

1483. **Chromatographic and electrophoretic analysis of commercial triphosphates and hexametaphosphates.** M. Lenzi and E. Mariana (Univ. Rome). *Rass. Chim.*, 1959, **11** (3), 11–15.—The chromatographic methods of Ebel and Volmar (*Compt. Rend.*, 1951, **233**, 415) and of Ebel (*Ibid.*, 1952, **234**, 621; Volmar *et al.*, *Ibid.*, 1952, **235**, 372) were found to be most suitable for the analysis of commercial triphosphates and allow a neat separation of di- and tri-phosphates. The technique of Grunze and Thilo (*Die Papierchromatographie der Kondensierten Phosphate*, Akademie-Verlag, Berlin, 1954) was found the most satisfactory; S. & S. 2043 paper gave the best results, and an acid medium (75 ml of isopropyl alcohol, 25 ml of H_2O, 5 g of trichloroacetic acid and 0·3 ml of 20% aq. NH_3) gave results superior to an alkaline medium (30 ml of isobutyl alcohol, 30 ml of 95% ethanol, 39 ml of H_2O and 1 ml of 25% aq. NH_3) at 20° for 25 hr. In the former case, the R_F values were—orthophosphate, 0·7; pyrophosphate, 0·42;

triphosphate, 0·31; trimetaphosphate, 0·26; tetraphosphate, 0·23; and tetrametaphosphate, 0·12; in the latter case, the R_F values were—trimetaphosphate, 0·71; tetrametaphosphate, 0·63; orthophosphate, 0·44; pyro- and tri-phosphate, 0·35; thus, the successive use of both methods in two-dimensional chromatography improves separation. Electrophoresis was carried out on Whatman No. 3 paper (9 cm × 45 cm), compressed between glass plates, with a potential difference of 1000 V for 1 hr. or more. At pH 8·5 (borax - H_3BO_3 - NaCl buffer) the displacement in cm per min. was 0·55 for trimeta-, 0·39 for tetrameta-, 0·43 for ortho-, 0·33 for tri- and tetra-, and 0·26 for pyro-phosphate. The lack of separation between the higher polyphosphates is not objectionable in the case of commercial triphosphates. CHEM. ABSTR.

1484. **Determination of small amounts of arsenic in organic matter.** The Metallic Impurities in Organic Matter Sub-Committee of The Analytical Methods Committee of The Society for Analytical Chemistry. *Analyst*, 1960, **85**, 629–643.—Two methods are recommended, each being preceded by destruction of the organic matter by wet oxidation. In the molybdenum blue method, the As is extracted with diethylammonium diethyldithiocarbamate soln. in $CHCl_3$ and converted into the molybdoarsenate complex, which is then reduced by means of hydrazine sulphate to a molybdenum blue complex for spectrophotometric determination at 840 mμ. In the second method, the As is separated by distillation as $AsCl_3$, and determined by a modification of the Gutzeit method. Collaborative work on the first method is described and the procedures for both methods are given in detail. The molybdenum blue method can give consistently accurate results for the As content of organic matter in the range 1·5 to 15 μg of As, and with specially purified reagents the lower limit of the range can be extended to 0·5 μg. Interference by Si and P is avoided and by Ge is unlikely. The Gutzeit method, being dependent on the assessment of a coloured stain, is recommended only as an approximation, and is particularly useful when it is necessary to determine whether or not the As content exceeds a certain limit. A. O. JONES

1485. **Separation of radioactive arsenic from germanium irradiated with protons.** K. Saito, S. Ikeda and M. Saito (Inst. for Nuclear Study, Tokyo Univ., Tanashi). *Bull. Chem. Soc. Japan*, 1960, **33** (7), 884–887.—The separation of almost carrier-free arsenic from germanium irradiated with protons, by distillation and by solvent extraction with diethyldithiocarbamate, is described. Total arsenic recovery was 94% and > 90%, respectively. The use of an acetate buffer was not found essential. Impurities in the final product, including carrier arsenic, are less than 10 μg for 0·4 mC, the specific activity for ^{74}As being ≃ 1 mC per 25 μg immediately after preparation. The over-all yield for ^{74}As is ≃ 70%. E. M. MAYES

1486. **The use of dithizone as internal indicator in titrimetry by precipitation. V. Direct volumetric determination of arsenate as bismuth arsenate.** M. Vancea and M. Voluşniuc (Inst. Chem., Acad. R.P.R. Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1959, **10** (2), 291–293.—The method is based on the titration of AsO_4^{3-} in the cold with a soln. of $Bi(NO_3)_3$ containing < 2% of free HNO_3, with dithizone as internal indicator, until the indicator changes from green to clear grey. H. SHER

1487. **New colorimetric applications of the chromate - o-dianisidine system. I. Indirect colorimetric determination of antimony(III), hyposulphite, hydrazine, hydroxylamine and hydrogen peroxide.** F. Buscaróns, J. Artigas and C. Rodriguez-Roda (Fac. of Sci., Univ., Barcelona, Spain). *Anal. Chim. Acta*, 1960, **23** (3), 214–216 (in English).—The method consists in the oxidation of the compounds or ions named with an excess of K_2CrO_4. This excess is determined by measuring the extinction of the red colour formed by the reaction of *o*-dianisidine with chromate in acid soln. The oxidation products of the substances named do not interfere. *Procedure*—Potassium chromate soln. (200 μg per ml) (2 ml) is transferred to a 100-ml flask and the test soln. is added, followed by 3 ml of 5N-H_2SO_4. The mixture is set aside to complete the reaction, and 0·5 ml of reagent soln. (0·5 g of *o*-dianisidine dissolved in 50 ml of acetone and diluted to 100 ml with water) is added. The soln. is diluted to volume with water and the extinction at 470 mμ is read between 5 and 30 min. after the addition of the reagent. Results are referred to an appropriate calibration curve. The procedure is suitable for concn. from 0·1 to 4 μg per ml. H. M.

1488. **Rapid gravimetric determination of bismuth as bismuth oxalate.** M. Vancea and M. Voluşniuc (Inst. Chem., Acad. R.P.R., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1959, **10** (2), 283–286.—Tervalent Bi is pptd. from dil. HNO_3 soln. with 0·1N-oxalic acid. Since the ppt. is insol. in 2% HNO_3, the method can be used in the presence of Ag, Pb, Cu, Fe, Co and Ni. The max. error for 5 mg of Bi per ml is ± 0·2%. H. SHER

1489. **The use of dithizone as internal indicator in precipitation titrimetry. I. Direct volumetric determination of bismuth as bismuth phosphate.** M. Vancea and M. Voluşniuc (Inst. Chem., Acad. R.P.R., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1959, **10** (2) 269–273.—A soln. containing ≃ 0·5% of Bi (10 to 20 ml) in 2% HNO_3 is titrated with 0·1N-KH_2PO_4 in the presence of 1 ml of a 0·03% soln. of dithizone in $CHCl_3$. At the end-point the orange Bi dithizonate changes through grey to green.

III. Direct volumetric determination of bismuth as bismuth arsenate. M. Vancea and M. Voluşniuc. *Ibid.*, 1959, **10** (2), 279–281.—The same procedure is adopted with the use of 0·04M-Na_3AsO_4.

IV. Direct volumetric determination of bismuth as bismuth oxalate. M. Vancea and M. Voluşniuc. *Ibid.*, 1959, **10** (2), 287–290.—Approximately 10 to 20 ml of a soln. of $Bi(NO_3)_3$ is treated with 5 ml of acetic acid - Na acetate buffer soln. (pH 4·5) and 1 ml of a 0·03% soln of dithizone in $CHCl_3$. The mixture is titrated with 0·1N-oxalic acid to a green colour. H. SHER

1490. **Liquid-metal fuel-reactor experiment—spectrographic methods for bismuth analysis.** C. H. Anderson and D. W. Brown (Babcock and Wilcox Co., Research Center, Alliance, Ohio, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. BAW-1091, 1960, 36 pp.—Development of a rapid control method for Mg and Zr that have been added as corrosion inhibitors to a circulating bismuth loop is described. A rapid method of determining the amount of corrosion products in liquid bismuth is

also reported. Magnesium and Zr can be quickly determined in 10% (w/v) bismuth in 8N-HNO_3 over the 100 to 600 p.p.m. range through the use of a rotating disc technique. Coeff. of variation of 2·4% for the Mg and 2·9% for the Zr determination were observed. It was found that Mg concn. up to 10,000 p.p.m. had no effect on the Zr determination. Some corrosion products were determined by d.c. arc excitation on an ignited Bi_2O_3 sample. Adequate precision was attained and there was good agreement between the spectrographic and chemical determinations of Fe and Cr. Modifications to the basic methods were briefly investigated. NUCL. SCI. ABSTR.

1491. **Extraction and flame-spectrophotometric determination of vanadium.** C. M. Stander (African Metals Corp. Ltd., P.O. Box 66, Meyerton, Transvaal, S. Africa). *Anal. Chem.*, 1960, **32** (10), 1296–1299.—After electrolysis at a mercury cathode to remove Cu, Fe, Sn and Mo, V is extracted from dil. H_2SO_4 soln. with cupferron and ethyl acetate. The extract is diluted to 40 ml and aspirated into the burner of a Beckman DU flame spectrophotometer. The intensity of the emission of V at 529 or 550 mμ is referred to a standard curve. Tolerance limits are quoted for 11 elements.

T. R. ANDREW

1492. **Spectrophotometric determination of vanadium as molybdovanadic acid.** G. W. Wallace and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 355–362 (in English).—At pH values between 1·5 and 6·0, V^V reacts with MoO_4^{2-}, to form 5-molybdovanadic acid (Mo to V ratio = 5:1), with maximum formation at pH 3·0 to 3·5, and having a strong absorption at 360 mμ (extinction 0·74 in 1-cm cell for 0·5 mg of V per 50 ml). The interference of 31 ions has been studied; AsO_4^{3-}, Ba^{2+}, Bi^{3+}, citrate, $Cr_2O_7^{2-}$, Fe^{3+}, GeO_4^{2-}, oxalate, Pb^{2+}, SiO_3^{2-} and tartrate must be absent. Results on three standard steel samples, after prior removal of Fe, Cr and Si, were within 3% of the stated values.

T. R. ANDREW

1493. **Separation of niobium, tantalum, titanium and zirconium from each other.** A. K. Majumdar and A. K. Mukherjee (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **23** (3), 246–247 (in English).—The acidified soln. containing Nb, Ta, Ti and Zr is digested on a water bath with a large excess of 5% pyrogallol soln. and set aside over-night. The ppt. of Nb and Ta pyrogallates is filtered off, washed with weak pyrogallol soln., dried and ignited. The residue is fused with $KHSO_4$, then dissolved, and the procedure is repeated to effect complete separation of Nb and Ta from Ti and Zr. The mixed oxides of Nb and Ta are separated by the *N*-benzoyl-*N*-phenylhydroxylamine method (*Ibid.*, 1958, **19**, 23; 1959, **21**, 245). The filtrates and washings are evaporated almost to dryness and the organic matter is destroyed by wet oxidation with conc. HNO_3, concn. H_2SO_4 and $HClO_4$. The soln. is cooled and diluted, and the Zr is pptd. with salicylhydroxamic acid in the presence of H_2O_2 (*Ibid.*, 1960, **22**, 25). The Ti is pptd. from the filtrate with cupferron after boiling to destroy H_2O_2 (Majumdar and Chowdhury, *Anal. Abstr.*, 1957, **4**, 450).

1494. **Volumetric determination of small amounts of oxygen.** E. S. Boichinova, S. M. Efros and V. D. Nemirovskiĭ. *Trudy̆ Leningr. Tekhnol. Inst. im. Lensoveta*, 1959, (58), 31–35; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,119.—The method is based on the oxidation of Ti^{3+} to Ti^{4+} and titration of unchanged Ti^{3+} with $FeCl_3$ soln. The rate of reaction between O and Ti^{3+} increases with increase of pH, but even in alkaline medium the rate is not sufficiently high for the O to be completely absorbed by a single passage of the gas through the absorbent soln. A closed system is used, comprising an absorbing vessel and two gas pipettes with pressure vessels. The gas sample is passed from the feed gas pipette through the absorbing vessel to the receiving gas pipette and then back to the feed pipette. Pure N is first passed through the system, then to the absorbing vessel are added 25 to 30 ml of standard $TiCl_3$ soln. in N-HCl and 10 to 15 ml of a satd. $CaCl_2$ soln., followed by excess of 3N-alkali (60 to 70 ml). The gas sample is passed through the absorbing vessel till absorption is complete (5 or 6 cycles); 3N-HCl is then added dropwise to dissolve the ppt. (a slight haze of TiO_2 may remain), 0·5 ml of 20% NH_4SCN soln. is added with the acid, and the unchanged Ti^{3+} are titrated with $FeCl_3$ soln. The method can be used for mixtures containing 0·1 to 1% of O. The error is $\not>$ 2%.

C. D. KOPKIN

1495. **Method and apparatus for analysing a reactive gas [to determine its content of hydrogen sulphide].** Standard Oil Co. [Inventors: E. B. Offutt and L. V. Sorg]. Brit. Pat. 849,456; date appl. 24.5.57.—In a method for continuously and automatically determining the hydrogen sulphide concn. in air directly, without interference from other common sulphur-containing contaminants, *e.g.*, thiols and sulphur dioxide, a sample of the air is saturated with water and then applied under precise conditions to a moving transparent tape having a hydrogen sulphide-sensitive coating (film of gelatin impregnated with Pb acetate and Na acetate) which darkens in a quant. manner on exposure to hydrogen sulphide. The extent to which the light transmittancy of the film is reduced as it moves continuously through the exposure chamber is measured by means of a photo-electric cell located below the tape, the variations in the electrical response from the cell in accordance with the variations in the concn. of hydrogen sulphide in the gas sample being transmitted to a recorder.

J. M. JACOBS

1496. **Indirect colorimetric determination of sulphide and cyanide with thiofluorescein.** M. Wroński (Dept. Chem. Technol., Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 457–460.—Alkaline soln. of thiofluorescein, decolorised with $AgNO_3$, become blue on the addition of H_2S or HCN. This phenomenon is used to determine H_2S (0·5 to 2 μg) and HCN (1 to 7 μg). The $AgNO_3$ - thiofluorescein reagent (**I**) is prepared by adding thiofluorescein soln. (5 mg in 50 ml of 0·1N-aq. NH_3) dropwise to 50 ml of 2 $\times$ 10^{-4}N-$AgNO_3$ until a permanent blue colour appears, then adding 20 ml of N-aq. NH_3 and diluting to 500 ml. A soln. of 2 g of As_2O_3 in 25 ml of N-NaOH treated with 5 g of Na_2CO_3 and 10 ml of conc. aq. NH_3 and diluted to 1 litre is used as a combined absorbent and diluent (soln. *A*). The determination is carried out by mixing 5 ml of sample with 5 ml of **I**, diluting to 12 to 25 ml with *A*, and measuring the extinction after 2 min. A blank and calibration standard are prepared at the same time. For the simultaneous determination of H_2S and HCN, after the extinction has been measured, a drop of

formaldehyde soln. is added to discharge the colour due to HCN, and the extinction due to H_2S alone is measured after 10 min. P. BRYCH

1497. **Spectrophotometric study of the Schiff reaction as applied to the quantitative determination of sulphur dioxide.** R. V. Nauman, P. W. West, F. Tron and G. C. Gaeke, jun. (Dept. Chem., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1307–1311.—A study of the u.v. and visible spectra of the several products of the reactions between SO_2, formaldehyde, pararosaniline and HCl has been carried out. It is concluded that the purple reaction product is not a Schiff base, but a pararosaniline methylsulphonic acid. T. R. ANDREW

1498. **Determination of sulphur dioxide and chlorate when present together.** I. E. Flis and T. A. Tumanova (Leningrad Technol. Inst.). *Zavod. Lab.*, 1960, **26** (8), 943–945.—The SO_2 is oxidised by a soln. of H_2O_2 of known concn. and the excess is determined by titration with a soln. of $KMnO_4$. The ClO_3^- are then determined by heating the soln. with excess of $FeSO_4$ soln., and titrating the excess with $KMnO_4$ soln. G. S. SMITH

1499. **New methods of control in bisulphite manufacture.** G. V. Zavarov (M. I. Kalinin Chernorechensk Chem. Works). *Zavod. Lab.*, 1960, **26** (8), 940–943.—To determine the relative amounts of sulphite and bisulphite in a soln. it is possible to use the soln. both as titrant and soln. being titrated. About 1 ml of the soln. containing $(NH_4)_2SO_3$ and NH_4HSO_3, of concn. corresponding to $\simeq$ 500 g of SO_2 per litre, is diluted to 100 ml with 0·05% EDTA (disodium salt) soln. (to prevent oxidation by the air), and 20 ml is poured into 10 ml of KIO_3 - KI soln. prepared by adding 2·5 g of KI and 1 ml of 0·01N-H_2SO_4 to 100 ml of a soln. of 25 g of KIO_3 in 1 litre. The soln. is treated with 1 g of $Na_2B_4O_7.10H_2O$ and the iodine liberated in the first reaction—

$$2NH_4HSO_3 + KIO_3 + KI = I_2 + K_2SO_4 + (NH_4)_2SO_4 + H_2O,$$

is titrated with the diluted sample soln., with starch as indicator, the reaction being—

$$(NH_4)_2SO_3 + I_2 + H_2O = (NH_4)_2SO_4 + 2HI.$$

G. S. SMITH

1500. **Determination of sulphate ions by direct titration with lead nitrate using diphenylcarbazone indicator.** G. N. Nechiporenko. *Gidrokhim. Materialÿ*, 1959, **29**, 214–218; *Ref. Zhur., Khim.*, 1960, (15), Abstr. No. 61,098.—The procedure for the direct titration of SO_4^{2-} (*Anal. Abstr.*, 1958, **5**, 2008) is modified. Interference by heavy metals is suppressed by adsorption with a cation-exchange resin. With samples containing 0·01 and 0·025 mg of SO_4^{2-} the errors are $\not>$ 3% and 2%, respectively. With concn. of 25 to 100 mg of SO_4^{2-} per litre, micro-titration is recommended. Samples containing < 10 mg of SO_4^{2-} per litre should first be treated with the cation-exchange resin and evaporated. The method may be used for the determination of SO_4^{2-} under field conditions. K. R. COOK

1501. **Ultra-violet spectrophotometric determination of trace amounts of selenium with o-phenylenediamine.** Hisae Ariyoshi, Michio Kiniwa and Kyoji Tōei (Fac. Sci., Univ., Okayama, Japan). *Talanta*, 1960, **5** (2), 112–128 (in English).—Selenium reacts with *o*-phenylenediamine at pH 1·5 to 2·5 to give piaselenole, which can be extracted into toluene and determined by u.v. spectrophotometry. *Procedure*—To the sample soln. containing $\not>$ 30 μg of Se add a small amount of 80% formic acid and dilute to 50 ml with water. Adjust the pH to 1·5 to 2·5, add 0·2% *o*-phenylenediamine soln. (2 ml) and set aside for 2 hr. Extract with toluene (10 ml), centrifuge and measure the extinction of the toluene layer at 335 mμ; Al, NH_4^+, Sb, As, Ba, Cd, Ca, Cr, Co, Cu, Pb, Mg, Mn, Ni, K, Na, NO_3^-, SO_4^{2-}, PO_4^{3-} and tartrate do not interfere, but Bi, Sn and I^- must be absent. Interference from Fe^{III} can be prevented by the addition of EDTA. W. T. CARTER

1502. **Extraction of chromium(III) with 2-thenoyltrifluoroacetone. Direct spectrophotometric determination in the organic phase.** S. K. Majumdar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chem.*, 1960, **32** (10), 1337–1339.—At pH $\simeq$ 6, Cr^{3+} react with 2-thenoyltrifluoroacetone in benzene to form an orange benzene-sol. chelate. The extraction is 100% at pH 5·75, 70% at pH 5 and 50% at pH 6·7, after shaking for 15 min. Of 13 ions examined, Ag^+ and Al^{3+} may be tolerated at levels up to twice that of the Cr^{3+}. The extinction is measured at 430 mμ. T. R. ANDREW

1503. **Determination of chromate in the presence of arsenate or permanganate.** Á. Kellner, L. G. Molnár and L. Szekeres (Chem. Dept., Agric. Univ., Budapest). *Magyar Kém. Lapja*, 1960, **15** (9), 426–427.—Volumetric methods are described. *Procedure for the determination of chromate in the presence of arsenate*—The soln. is treated with 0·1N-KBr in H_2SO_4 medium. The reduction of chromate is complete in $\simeq$ 15 min.; KI and starch soln. are then added and the mixture is titrated with standard arsenite soln. *Procedure for the determination of chromate in the presence of permanganate*—The reduction of permanganate to MnO_2 is carried out with Na_2CO_3 and H_2O_2. The excess of H_2O_2 is destroyed by heating on a water bath, the soln. is acidified with H_2SO_4 and KI is added. The liberated iodine is titrated with standard $Na_2S_2O_3$ soln. The procedure is rapid, but correction factors must be applied. B. VASZKO

1504. **Process and apparatus for potentiometrically measuring and reducing chromate ions in aqueous solution.** Deutsche Gold- und Silber-Scheideanstalt, vormals Roessler. Brit. Pat. 853,326; date appl. 9.5.58. Germany, date appl. 25.5.57.—The potentiometric determination of extremely small quantities of chromate in waste liquors can be carried out with the aid of a measuring electrode, if necessary in the absence of quinhydrone, and the addition of the usual reducing agents, *e.g.*, $NaHSO_3$ or SO_2, is thereby controlled. The measurement is advantageously carried out in a small partial stream, which is branched off from the solution to be treated and fed to a measuring station, from which it is returned again to the main stream. J. M. JACOBS

1505. **Compounds of quinquevalent molybdenum with 8-hydroxyquinoline and their analytical uses.** A. I. Busev and Chzhan Fan (Lomonosov Univ., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 455–462.—Quinquevalent Mo forms two compounds with 8-hydroxyquinoline: a greenish-yellow ppt. produced at room temp. and a black ppt. produced in a boiling soln. The composition of the greenish-yellow ppt. corresponds approx. to the

formula $H_2Mo_4O_{11}(C_9H_7NO)_7.11H_2O$ and that of the black ppt. corresponds exactly to the formula $Mo_2O_3(C_9H_6NO)_4.H_2O$. The black compound of Mo^{5+} can be used for the photometric determination of small amounts of Mo (0·1 µg per ml) in a 50% acetone medium. The method gives accurate results and Ca, Mg, Cd, Ni, Zn and small amounts of Fe^{3+} and Cr^{3+} do not interfere. *Procedure*—Add conc. HCl (4 ml) to a neutral or slightly acid soln. containing $\not>$ 0·8 mg of Mo^{6+}. Dilute the soln. to 13 to 15 ml, heat it on a boiling-water bath and slowly add an aq. reducing soln. (0·1 g of hydrazine dihydrochloride per ml) (5 to 7 ml); continue heating for 10 to 20 min. Add 3% 8-hydroxyquinoline soln. in dil. acetic acid (4 ml) to the hot soln. while stirring and then aq. NH_3 soln. until a ppt. appears. Then add acetate buffer soln. (2 ml) at pH 4 and heat for 10 to 15 min. on a boiling-water bath. Cool the mixture to room temp., add acetone (25 ml) and dilute the soln. to 50 ml. Stir well and measure the extinction at 530 mµ. K. R. Cook

1506. **Determination of molybdenum in nitrilotriacetic acid medium by derivative polarography. Application to solutions of mixed thorium - uranium oxides.** D. L. Manning, R. G. Ball and O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1247–1250.—The effect of a number of complexing agents on the $E_{\frac{1}{2}}$ of U^{VI} and Mo^{V} is reported. Maximum separation ($E_{\frac{1}{2}}$ = − 0·23 V for U^{VI} and − 0·48 V and − 0·64 V for Mo) is obtained in a medium 0·15M in nitrilotriacetic acid at pH 3·0. Interferences have been studied at the level of 70 µg of Mo; 100 µg of Cr, Cu, Ti and Ni, 500 µg of Fe, 1 mg of U or 25 mg of Th may be present in 10 ml without causing an error greater than that implicit in the method (coeff. of variation ≃ 6%). T. R. Andrew

1507. **Determination of molybdenum and tungsten by an acidimetric method.** A. I. Lazarev (Akmolinsk Agric. Inst.). *Zavod. Lab.*, 1960, **26** (8), 935–938.—The method is based on potentiometric titration of the soln. in a vessel of antimony, which serves as the working electrode, with a reference silver - silver chloride electrode which serves also as a stirrer. G. S. Smith

1508. **Chemical - spectrographic determination of small amounts of molybdenum and tungsten in minerals.** L. I. Pavlenko (Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 463–466.—When the concn. of Mo and W is $< 10^{-4}$%, an enrichment is carried out before spectrographic determination with a d.c. arc. The sample (10 mg), a mixture of 2 mg of the residue obtained after chemical enrichment of the mineral by means of organic co-precipitants with silicate base (18 mg), is completely volatilised from the crater of a carbon electrode (depth 2·5 mm and diam. 3·5 mm). The slit width is 0·02 mm, the current 10 amp., and the exposure time 2·5 min. The spectra are photographed with type-II plates and sensitivity 8 or 11 units (GOST) for Mo, and 22 units (GOST) for W; the lines used are 3170·35 A (Mo) and 4294·6 A (W). Calibration curves are constructed by using the triple-standard method for log *R* *vs.* log *C*, where *R* is the relative intensity of the test line in comparison with the background and *C* is the concn. (%) of the test element. To prepare standards, MoO_3 and WO_3 are introduced into the base. When the mineral contains $> 10^{-4}$% of Mo and W, the determination is carried out by direct spectrographic determination. The sensitivities of the chemical - spectrographic determination of Mo and W are 2×10^{-6}% and 3×10^{-5}%, respectively. K. R. Cook

1509. **Spectrophotometric determination of molybdenum in alloys in the presence of tungsten, silicon and aluminium.** I. P. Kharlamov, P. Ya. Yakovlev and M. I. Lÿkova. *Zavod. Lab.*, 1960, **26** (8), 933–934.—The sample (0·1 to 0·5 g), together with 0·1 g of Fe if the alloy is based on Ni, Co or Cr, is dissolved in 50 ml of conc. HCl followed by 3 to 5 ml of conc. HNO_3 for oxidation, and the cooled soln. is treated with 10 ml of conc. H_2SO_4 and evaporated twice to fuming. The cooled residue is dissolved in 80 ml of water and the soln. is poured gradually into 100 ml of boiling 25% NaOH soln. After dilution of the cooled soln. to 500 ml it is set aside for 1 to 2 hr. An aliquot (250 ml) of the filtered soln. is treated with H_2SO_4 (1:4) until the pH is between 6 and 8, and then diluted to 500 ml. The extinction of the soln. is measured at 230 mµ, and the content of Mo is calculated by use of a calibration curve and a blank test. The method gave satisfactory results over the range 1 to 10% of Mo. G. S. Smith

1510. **Determination of tungsten and molybdenum without their separation.** E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte, Tirol, Austria). *Chemist Analyst*, 1960, **49** (3), 68–69.—Tungstate and molybdate are determined together by pptn. titration with Pb soln. and Mo is determined separately by titration with EDTA. *Procedures*: (*i*) *For W and Mo*—Acidify the soln. (approx. 0·8 millimole of W and Mo) with HNO_3 (1:1) and boil. Buffer at pH 6·8 with hexamine. Add 5 to 10 drops of 0·1% aq. 4-(2-pyridylazo)-resorcinol soln. and titrate the boiling soln. (300 to 400 ml) at a rate of 1 drop per sec. with 0·1M-$Pb(NO_3)_2$ to a permanent red colour. (*ii*) *For Mo* (0·05 to 0·2 *millimole*)—Add a known vol. of 0·05M-EDTA (disodium salt), tartaric acid (5 g), hydrazine sulphate (2 to 3 g) and H_2SO_4 (1:1) (2 ml). Dilute to ≃ 170 ml, boil for 5 min. and adjust the pH to 4 to 5 with aq. NH_3. Add 80 ml of methanol and 5 to 8 drops of 0·1% ethanolic 1-(2-pyridylazo)-2-naphthol soln. Titrate with 0·05M-$CuSO_4$ and finally restore the yellow colour by back-titration with EDTA. For 5 to 50 mg of Mo, a photometric determination at 450 mµ is described. P. D. Parr-Richard

1511. **Interference of iron in the determination of 12-tungstophosphoric acid with tri-n-butylamine.** C. C. Miller and D. H. Thow (Chem. Dept., Univ., Edinburgh, Scotland). *Talanta*, 1960, **5** (2), 128–130 (in English).—The interference of Fe^{III} in this method (*Anal. Abstr.*, 1960, **7**, 972) is due to the pptn. of $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}.nH_2O$. It can be prevented by reducing the Fe^{III} to Fe^{II} in a silver reductor, followed by pptn. of the complex from 2N-HCl. W. T. Carter

1512. **Procedure and problems in the fluorimetric determination of uranium.** T. Schönfeld, M. ElGarhy, C. Friedmann and J. Veselsky (Anorg. u. Phys. Chem. Inst., Univ., Wien, Austria). *Mikrochim. Acta*, 1960, (5–6), 883–897 (in German).—Uranium is determined in rocks, coal ash or leachings from coal ash by separating it from 8% HNO_3 soln. with ethyl acetate and transferring it

to a fluoride pellet for fluorescence measurement. Errors due to the properties of the pellet, to sample-vol. measurement and to the photometer are evaluated. Quenching by interfering elements is eliminated by solvent extraction followed by the method of standard addition. *Procedure*—For coal ash, evaporate the sample several times with HF and then with HNO_3 to give a soln. 8% in HNO_3. For alkali carbonate extracts, add HNO_3 to expel CO_2 and adjust to 8%. For H_2SO_4 extracts, precipitate SO_4^{2-} as $BaSO_4$; traces of Fe^{3+} or Al^{3+} prevent adsorption of U. Mix a 2-ml aliquot of the soln. with 10 ml of saturated $Al(NO_3)_3.8H_2O$ soln. (0·9 g per ml) and extract U with ethyl acetate (10 ml). Add 0·2 ml of extract to a pellet (NaF - LiF) (49:1) weighing 0·4 g, dry under a i.r. lamp and melt over a burner. Measure the fluorescence of the solidified melt, add a known amount of U, re-melt and measure again. For $< 20 \times 10^{-9}$ g of U per g of sample, concentrate the solvent extract and decant from the pptd. $Al(NO_3)_3$. P. D. Parr-Richard

1513. **Direct determination of uranium in concentrates by spectrophotometric titration with ferric sulphate.** T. M. Florence (Australian Atomic Energy Comm., Lucas Heights, N.S.W.). *Anal. Chim. Acta*, 1960, **23** (3), 282–288 (in English).—Uranium may be determined by reduction to U^{IV} and then titration with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln.; Cu, Mo and V interfere, and their maximum permissible concn. are discussed. The sample (50 to 100 mg of U_3O_8) is dissolved in $HClO_4$, diluted and acidified further with H_2SO_4 and diluted to 25 ml. A portion is transferred to a special reduction vessel (illustrated), and de-gassed with N. Bismuth amalgam is added and the vessel is shaken vigorously for 5 to 10 min. The special titration cell (illustrated) is placed in the spectrophotometer, 5 ml of water is added and the instrument is set at 650 mμ. Nitrogen is passed through, 5 ml of reduced soln. is added to the cell and the instrument is set to zero. The gas flow is then stopped and the extinction is measured. Nitrogen is passed through again, a little titrant (0·1N) is added, the gas flow is stopped and the extinction is again measured. This procedure is repeated to obtain a titration curve. H. M.

1514. **Determination of total uranium and uranium-235 in aluminium - uranium fuel elements.** W. L. Delvin, H. E. Palmer and U. L. Upson (General Electric Co., Hanford Atomic Products Operation, Richland, Wash., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. HW-57464, 1958. Decl. Apr. 1960. 22 pp.—Uranium - aluminium alloy fuel elements containing 3 to 5% of enriched U were analysed both for total U content and for the degree of enrichment ($\simeq$ 93% of ^{235}U). Each fuel element was reduced to wafers and turnings which were dissolved in HCl and Br. For the determination of total U, the U was reduced in a Jones reductor and re-oxidised with excess of standard $Ce(SO_4)_2$ soln., with subsequent back-titration of the excess of ceric ion with $FeSO_4$ soln. A correction for iron interference was necessary. The precision of this method is $\pm$ 0·3% at the 95% confidence level. For isotopic analysis, the uranium soln. were γ-counted in the 0·174 to 0·194-MeV interval, without chemical separation, and evaluated relative to mass-spectrometer-calibrated standards. Corrections for both U and $AlCl_3$ concn. were applied. Over-all counting precision is $\pm$ 0·4% or better. The reported isotopic concn. were derived from the determination of total U and the γ-counting results, and are precise to $\pm$ 0·5%. Nucl. Sci. Abstr.

1515. **Extraction of irradiated uranium by ketones in acid and acid-deficient solutions.** V. Veselý, H. Beranová and J. Malý (Inst. for Nuclear Research, Czech. Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (10), 2622–2629 (in German).—The extraction of uranium and its fission products from soln. 0·25M in $UO_2(NO_3)_2$ and 5M in NH_4NO_3 by a series of alkyl methyl ketones was found to vary with the concentration of free HNO_3 in nitrate soln. In the case of uranium this dependence is attributed to the formation of basic nitrates. of the type $[UO_2(OUO_2)_n].(NO_3)_2$, which, unlike $UO_2(NO_3)_2$, are not soluble in ketones. The partition coeff. of uranium decreases with decreasing acid concn.; its logarithm increases linearly with the logarithm of the carbonyl content of the ketone. The partition coeff. of the fission products varies similarly. The efficiency of the separation of uranium from its fission products can be expressed by the decontamination factor (DF), defined as the ratio $(A_v/C_v)/(A_0/C_0)$, where A_v and A_0 are the activities of 1 g of aq. phase and 1 g of organic phase, respectively, and C_v and C_0 are the corresponding concn. (w/w) of U. The DF is highest in soln. with a small acid deficiency (– 0·05M in free HNO_3) and lowest in neutral soln. and in those with a high acid deficiency; in strongly acid soln. it is greater than in neutral soln. In both acid and acid-deficient soln. the DF increases with increasing number of carbon atoms in the ketone. It is concluded that the separation of U from its fission products is best carried out by extraction with isobutyl methyl ketone from strongly acid soln. ($\simeq$ 3M in free HNO_3) or those with a small acid deficiency. R. M. Rowley

1516. **The mechanism of the extraction of uranyl nitrate by tributyl phosphate. II. Infra-red study.** K. Nukada, K. Naito and U. Maeda (Govt. Chem. Ind. Res. Inst. of Tokyo, Shibuya). *Bull. Chem. Soc. Japan*, 1960, **33** (7), 894–898.—The mechanism of the extraction of uranium by tri-n-butyl phosphate (TBP) is studied by means of i.r. spectra from Perkin - Elmer Model 12C and 321 spectrometers with rock-salt prisms. The systems TBP - water, TBP - nitric acid, TBP - uranyl nitrate, and TBP - uranyl nitrate - nitric acid are presented. It is concluded that the competitive extraction of both uranyl nitrate and nitric acid takes place during the process. E. M. Mayes

1517. **Application of gas - liquid chromatography to the analysis of corrosive gases. I. Development of apparatus and technique for separation of mixtures of chlorine trifluoride, hydrogen fluoride and uranium hexafluoride.** G. Iveson (Tech. Dept., U.K.A.E.A. Production Group, Capenhurst). U.K.A.E.A. Report PG82(CA), 1960. 23 pp.—Mixtures of UF_6, HF and ClF_3 may be separated with N or He as the carrier gas, a packing of "Kel-F" moulding powder [poly(chlorotrifluoroethylene)] and "Kel-F 40" polymer oil in a nickel column at 60°, and katharometer detection. The response was linear with concn. for ClF_3 and UF_6, but was non-linear for HF, the response increasing rapidly with increase in HF concn. The method is suitable for up to 25% by vol. of HF, 15% by vol. of ClF_3 and 15% by vol. of UF_6 in a sample vol. of $\simeq$ 20 ml at s.t.p. T. R. Andrew

1518. **Fluorimetric determination of uranium in zirconium and hafnium.** P. A. Vozzella, A. S. Powell, R. H. Gale and J. E. Kelly (Nuclear Div., Combustion Engineering Inc., Windsor, Conn., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1430–1433.—Uranium ($\simeq$ 1 p.p.m.) in Zircaloy or in pickling soln. is determined fluorimetrically in a Jarrell-Ash instrument after extraction from HNO_3 soln. into ethyl acetate. Results are accurate to within $\pm$ 5%. *Procedure*—Dissolve the Zircaloy (0·5 g) in water (10 ml) by adding 48% HF (2 ml), 30% H_2O_2 (9 drops) and conc. HNO_3 (5 ml). Evaporate to dryness, dissolve the residue in water, add conc. HNO_3 (1 ml), and dilute to 20 ml. To 2 ml of this soln. add satd. aq. $Al(NO_3)_3$ (15 ml) and solid $Al(NO_3)_3.9H_2O$ (0·5 g), and extract for 2 to 3 min. with ethyl acetate (5 ml). Pipette 0·4 ml of the organic phase on to four pellets (0·4 g each) of a flux of 98% of NaF and 2% of LiF. Fuse, cool, and measure the fluorescence. Determine the content of U by comparison with standards.

J. P. STERN

1519. **The determination of some impurities in high-purity uranium. The use of anion exchangers for the separations.** D. B. Stevančević (Inst. of Nucl. Sci. "Boris Kidrich," Beograd-Vinca). *Bull. Soc. Chim., Belgrade*, 1959, **23–24** (3–4), 185–190.—The determination of μg amounts of Cu, Cd, Zn, Ni, Co, Fe, Mn and Al in high-purity uranium is effected by isolating the total impurities from dil. H_2SO_4 (pH 1·5) on Dowex-1 resin, followed by elution with 6N-HCl (for Ni, Al and Mn), 0·5N-HCl (for Co, Cu and Fe) and 0·0005N-HCl (for Cd and Zn). A reproducibility of 5·2 to 15·2% for each element is attained. The method is applied to the analysis of a sample of uranium peroxide.

M. G. SEAMAN

1520. **Determination of trace amounts of cadmium in uranyl nitrate with dithizone.** A. Golkowska (Inst. for Nucl. Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (3), 389–394.—*Procedure*—Dissolve 0·2 g of uranyl nitrate in water, transfer to a 50-ml separating-funnel, add 2 ml of 17% ammonium carbonate soln., mix and add 1 ml of conc. aq. NH_3. Extract with 10-ml portions of dithizone soln. (0·002% in CCl_4) till the extracting layer is green, then extract with a 5-ml portion. Wash the combined extracts with 20 ml of water, then shake them with 10 ml and 5 ml of 0·01N-HCl. Wash the acid extract with 3 ml of dithizone soln. and then with 5 ml of CCl_4. To the acid extract add 5 ml of 10% citric acid soln., 5 ml of dithizone soln. (0·005% in CCl_4) and 5 ml of 20% NaOH soln. Shake for 1 to 2 min. and filter through cotton wool into a 1-cm cell. Measure the extinction at 520 mμ against a blank and refer the result to a calibration graph. The dithizone - Cd complex showed no change in extinction during 2 hr. The accuracy was not affected by a fivefold excess of Ag^+, Bi^{3+}, Cu^{2+}, Hg^+, Ni^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+} or Co^{2+} individually, nor by the combined addition of a 2·5-fold excess each of Zn^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+}, Cu^{2+} and Co^{2+}. The errors were $\not>$ 5% in the range 1 to 10 μg of Cd, increasing to 10% in the 0·1 to 0·5-μg range. The sensitivity can be increased to 0·1 μg of Cd per g of uranyl nitrate by taking up to 1 g of sample and proportionately increasing the amounts of ammonium carbonate and aq. NH_3 soln.

P. BRYCH

1521. **Determination of aluminium in pure uranium and in aluminium - uranium alloys (8-hydroxyquinoline spectrophotometric procedure).** C. O. Granger (U.K.A.E.A., Development and Engineering Group, Culcheth). U.K.A.E.A. Report DEG 219(C), 1960. 17 pp.—The development of the method is described. The sample, containing up to 5 g of U, is dissolved in HCl and H_2O_2. Thioglycollic acid, EDTA, carbonate buffer soln., cyanide and 8-hydroxyquinoline (**I**) are added; after 1 hr. the Al is extracted as its complex with **I** into $CHCl_3$. The extinction of the soln. at 390 mμ is measured and the content of Al is derived from a calibration graph obtained by using known amounts of Al. If the alloy contains Ti, V or Zr, these are extracted as complexes with *N*-benzoyl-*N*-phenylhydroxylamine before the normal procedure is applied. Full details are appended. The standard deviation for contents of Al up to 50 μg is $\pm$ 0·3 μg.

G. J. HUNTER

1522. **Determination of free acid in plutonium solutions.** J. L. Pflug and F. J. Miner (Rocky Flats Plant, Dow Chemical Co., Denver, Colo., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 362–367 (in English).—An investigation was made of the use of K oxalate, K tartrate and Na citrate as complexing agents to prevent hydrolysis and pptn. of Pu during potentiometric titration of free acidity. The use of Na citrate at pH 8·0 to 9·0 is recommended; after addition of the sample soln. the soln. is titrated potentiometrically to the original pH.

T. R. ANDREW

1523. **Analysis of halogen mixtures by microdiffusion in combination with isotope-dilution technique.** K. J. Öbrink and M. Ulfendahl (Univ. Uppsala, Sweden). *Acta Soc. Med. Upsaliensis*, 1959, **64**, 384–391.—A modification of the microdiffusion method of Conway is described for the separate determination of Cl, Br and I. Analysis of some mixtures of two halogens is possible, but determination of Cl or I in bromine is not possible. By the conventional procedure for microdiffusion analysis, only Br can be determined in a mixture of all three halogens. However, by combining microdiffusion analysis and the isotope-dilution technique it is possible to determine all three halogens in mixtures.

CHEM. ABSTR.

1524. **Determination of fluorine by neutron activation.** O. U. Anders (Radiochem. Lab., Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1368–1369.—The method described is based on the $^{19}F\,(n, \alpha)^{16}N$ reaction and can be used to determine 100 p.p.m. of F in a 1-g sample. To improve the sensitivity and statistical certainty of the method, a fast-transfer shuttle-rabbit system permits the use of multi-activation runs with cumulative counting.

K. A. PROCTOR

1525. **Colour reaction for fluoride ion.** H. Weisz (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Mikrochim. Acta*, 1960, (5–6), 703–705 (in German).—Use is made of the high stability of FeF_3 which is formed on addition of F^- to ferric rhodizonate in the presence of $AgNO_3$, the liberated rhodizonic acid yielding a blue-black Ag rhodizonate. Marked reaction is observed with 15 μg of F^- in 0·05 ml. Oxalate, S^{2-} and Ca^{2+} interfere; CrO_4^{2-}, PO_4^{3-}, salicylate and sulphosalicylate reduce the sensitivity. *Procedure*—To a drop of the neutral sample on a spot-plate

or on filter-paper add a drop of reagent [prepared by mixing 1% $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. (2 ml) with 1% $AgNO_3$ soln. (2 ml), adding Na rhodizonate until a ppt. forms, filtering, adding acetic acid (1 drop) and diluting to 10 ml with 1% $AgNO_3$ soln.]. A blue - black ppt. appearing within 1 min. indicates F^-. J. P. STERN

1526. **Determination of ionisable fluorides in gases.** Mine Safety Appliances Co. Brit. Pat. 851,270; date appl. 1.4.59. U.S.A., date appl. 4.4.58.—When a gas, *e.g.*, air, containing HF or other ionisable fluoride is brought into contact with an inert porous material (filter-paper) carrying, as reagent, a freshly prepared suspension in an aq. HCl medium (containing sugar or glycerol) of the reaction product of 4-arsono-4′-dimethylamino-azobenzene and an excess of $ZrOCl_2.8H_2O$ over a 1 : 1 mol. ratio, the reagent assumes a brown to deep-pink colour, the exact hue being dependent on the concn. of the fluoride in the gas being tested. With a vol. of 1 litre of gas as the sample, the reagent has a sensitivity of $\simeq$ 0·2 p.p.m. of hydrogen fluoride. J. M. JACOBS

1527. **Analysis of chlorine cell gas by gas chromatography.** E. E. Neely (Columbia-Southern Chem. Corp., Corpus Christi, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1382–1383.—The method described has been developed specifically for the analysis of chlorine cell gas, but is adaptable to any sample that requires a two-column separation. The gases are passed first through a 12-ft. column of 30% (w/w) Fluorolube grease (Type LG–160) on 30 to 50-mesh Chromosorb, and any gases unresolved are then passed through an 8-ft. Molecular Sieve column (Type 13X), 30 to 50 mesh. A thermal conductivity detector is used. C. B. BAINES

1528. **Volumetric assay of ammonium perchlorate.** E. A. Burns and R. F. Muraca (Jet Propulsion Lab., Inst. of Technol., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1316–1318.—*Procedure*—Dissolve 1·0 g in de-aerated water and dilute to 250 ml. Transfer 25 ml to a 500-ml conical flask containing 50 ml of HCl, and add 1 to 2 g of $NaHCO_3$ and 50 ml of 0·3N-$TiCl_3$. Add rapidly 1 ml of OsO_4 soln. (0·008M in 0·1N-H_2SO_4). Close the flask with a stopper carrying a tube leading to a flask containing 100 ml of 12N-HCl and connected to a third flask containing 100 ml of satd. $NaHCO_3$ soln. Boil the test soln. for 10 min. and cool to room temp. in an ice bath ($NaHCO_3$ soln. should be drawn back into the second flask so as to evolve CO_2). Titrate with 0·33N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$, with NH_4SCN as indicator. Standard deviations of 0·11 to 0·19 are quoted for 4 determinations on each of 3 samples of 99·3 to 99·8% purity. All soln. and the water used must be de-aerated by bubbling with N for 30 min. T. R. ANDREW

1529. **Impregnation method for the micro-determination of bromide and iodide.** A. J. Hłyńczak, J. S. Knypl and R. Antoszewski (Dept. of Physiol., Acad., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 407–411.—Micro amounts (1 to 30 μg) of bromide and iodide can be determined by placing a drop of the test soln. on filter-paper impregnated with Ag_3AsO_4, developing, fixing and measuring the area of the resulting spot. Mixtures give a double spot, with iodide at the centre, which permits the simultaneous determination of the two halides. Errors are < 5%. The method is suitable for the determinations of the specific radioactivity of samples containing ^{131}I, ^{82}Br and ^{80}Br. P. BRYCH

1530. **Detection of iodine compounds by paper chromatography.** J. M. Calvo and L. Bascur (School of Med., Univ., Santiago, Chile). *Nature*, 1960, **188**, 141–142.—The rapid fading of chromatograms caused by traces of iodine in the air when detecting inorganic and organic iodine-containing compounds by the $Ce(SO_4)_2$ - As_2O_3 reagent (Kolthoff and Sandell, *J. Amer. Chem. Soc.*, 1934, **56**, 1426) can be obviated by exposing the paper, immediately after development, to the vapour of 50% phenol soln. before drying in air. The iodine-containing compound is thereby fixed as a white spot on a dark-brown background. W. J. BAKER

1531. **Determination of periodate by the formaldehyde formed on oxidation of ethanediol.** L. Maros, I. Perl-Molnár and E. Schulek. *Magyar Kém. Foly.*, 1960, **66** (9), 342–344.—This is a version (in Hungarian) of the paper published (in German) in *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (4), 475 (*cf. Anal. Abstr.*, 1961, **8**, 562). B. VASZKO

1532. **Arsenate - iodimetric determination of manganese.** G. B. Shakhtakhtinskiĭ and R. A. Melikova. *Azerbaidzh. Khim. Zhur.*, 1959, (5), 63–69; *Ref. Zhur., Khim.*, 1960, (16), Abstr. No. 65,115.—The method is based on the pptn. of Mn^{2+} by an excess of AsO_4^{3-}, followed by the dissolution of the ppt. in acid and iodimetric titration of the liberated H_3AsO_4. K. R. COOK

1533. **Spectrophotometric determination of technetium(VII) with thioglycollic acid.** F. J. Miller and P. F. Thomason (Anal. Chem. Div., Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1429–1430.—The complex of Tc (4 to 20 μg) with thioglycollic acid (**I**) formed at pH 8·0 is determined absorptiometrically at 655 mμ. A tenfold excess of Cl^-, F^-, Br^-, I^-, PO_4^{3-}, SO_4^{2-} or tungstate does not interfere, but $Cr_2O_7^{2-}$, molybdate and ruthenate interfere. No accuracy is stated, but the reproducibility is within ± 2%. *Procedure*—To the soln. of $KTcO_4$, containing 10 to 200 μg of Tc, add M-Na acetate (1 ml) and 10% (v/v) **I** soln. (pH 8·0 ± 0·2) (1 ml). Heat at 100° for 15 min., dilute to 5 ml with water, and measure the extinction at 655 mμ against a blank. J. P. STERN

1534. **Chemical analysis on the microgram scale. VI. The ultra-micro gravimetric determination of technetium and rhenium.** F. Jasim, R. J. Magee and C. L. Wilson (Chem. Dept., Univ., Belfast, N. Ireland). *Mikrochim. Acta*, 1960, (5–6), 721–728 (in English).—The scheme previously described (*Talanta*, 1960, **4**, 17) for the separation of Tc, Re, Mn, Ru and Mo is adapted to ultra-micro gravimetry. The Tc and Re are pptd. and weighed as tetraphenylarsonium pertechnetate and perrhenate, respectively; 2 to 3 μg of Tc and Re can thus be determined with a standard deviation of ± 0·08 μg. J. P. STERN

1535. **Elimination of the effect of molybdenum on the colorimetric determination of rhenium.** B. S. Tsȳvina and N. K. Davidovich (State Sci. Res. and Development Inst. of the Rare Metals Industry). *Zavod. Lab.*, 1960, **26** (8), 930–932.—*Thiourea method* (*for contents of Re between* 0·001 *and* 0·1%)—The sample (0·3 to 2 g) is mixed with 3 to 4 g of CaO and heated at 650° to 700° for 2 hr.

The mass is boiled with 150 ml of water until the vol. is reduced to 100 ml (20 to 25 min.). The soln. is filtered through a Buchner funnel and the insol. matter is washed with hot water. The filtrate is treated with 5 ml of 10% $BaCl_2$ soln. and boiled until the vol. has been reduced to 80 ml or, if the content of Re is in the lower part of the range, to 35 ml. The ppt. is filtered off and washed with hot water. The filtrate is diluted to a suitable vol. and an aliquot (10 ml) is treated with 5 ml of conc. HCl, 2·5 ml of 10% thiourea soln. and 1 ml of 20% $SnCl_2$ soln., and then diluted to 25 ml. After 30 min. the extinction is measured with a violet filter. *Thiocyanate method* (*for contents of Re between* 0·0002 *and* 0·001%)—The sample (2 g) is heated with CaO (4 g) as described above and the mass is extracted with hot water and the soln. is filtered. The filtrate is treated with 5 to 6 ml of 10% $BaCl_2$ soln. and evaporated to 35 to 40 ml. The soln. is again filtered, and an aliquot (25 ml) is evaporated to between 7 and 8 ml. The soln. is treated with 10 ml of conc. HCl and the cooled and diluted soln. (20 ml) is treated with 1 ml of a soln. containing 10 mg of Fe as $FeCl_3$, 2 ml of 20% NH_4SCN soln. and 1 ml of 35% $SnCl_2$ soln. The soln. is diluted to 25 ml and the extinction is measured after 30 min. with a violet filter.
G. S. Smith

1536. **Specific spot test for iron.** K. Lal Mallik and Buddhadev Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge). *Anal. Chim. Acta*, 1960, **23** (3), 225–226 (in English).—Two methods are described. *Procedure* (*i*)—One drop of test soln. is mixed on a spot-plate with a few crystals of a reducing agent (*e.g.*, ascorbic acid, hydroxyammonium chloride or $Na_2S_2O_5$), followed by 2 drops of reagent soln. (1% of phenyl 2-pyridyl ketoxime in 95% ethanol). The soln. is made alkaline with 0·5M-aq. Na_2CO_3 or 6M-aq. NH_3. A violet colour indicates the presence of Fe. *Procedure* (*ii*)—One drop of test soln. is placed on Whatman No. 40 paper, followed by two drops of 10% aq. ascorbic acid soln. and two drops of reagent soln. The spot is exposed to NH_3 vapour. A violet coloration indicates the presence of Fe. The only ions that interfere are Cu^{2+} and Co^{2+} (in amounts > 10 times that of the Fe). Cyanide inhibits the test. The limit of identification is 0·05 μg and the limit of dilution is 1 in 10^6.
H. M.

1537. **Test for iron by automatic concentration in a small area of reagent.** F. L. Hahn. *Mikrochim. Acta*, 1960, (5–6), 675–677 (in German).—The test for Fe^{3+} has a limiting concn. of 0·06 μg per ml and requires highly pure Fe-free NH_4SCN. *Procedure*—Prepare the reagent as follows: to 5% aq. succinic acid (20 ml) at pH 4·2 add NH_4SCN (25 g) and then $K_4Fe(CN)_6$ (0·4 g) and dilute to nearly 100 ml; add $ZnSO_4$ (0·5 g), make up to 100 ml, and, after some time, filter. Add 10 ml of this reagent to the aq. sample (60 ml) covered with ether (30 ml). In the ether suspend the test paper freshly impregnated with $\simeq$ 0·01 ml of 1% $K_4Fe(CN)_6$ soln. followed by $\simeq$ 0·01 ml of 1% $ZnSO_4$ soln. Stir for 30 to 60 min. If $\simeq$ 3·6 μg of Fe is present the test spot turns blue; it is unaffected by 1·8 μg of Fe.
J. P. Stern

1538. **Determination of iron by the impregnation method.** A. Dorożalska. *Prace. Kom. Mat.-Przyr. Poznań, Tow. Przyj. Nauk*, 1959, **7** (9), 43–49; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,079.—In the impregnation method, an element is determined by the area of the coloured spot formed when a known volume of the test soln. is placed on paper saturated with an insoluble reagent. This method can be used to determine many elements with an error of $\simeq$ 2% and has many advantages over normal paper chromatography, the error of which is 10 to 30%. The determination of small amounts of Fe^{3+} is described. The impregnated paper is prepared by immersing 8-cm strips of ashless filter-paper in 0·03N-$K_4Fe(CN)_6$ to a depth of $\simeq$ 2 mm. When the soln. reaches the upper edge of the strip, the paper is removed, dried at 60°, steeped in 0·03N-$Zn(NO_3)_2$, washed with water, again dried, and cut into 1·5-cm strips. The test soln. (0·001 to 0·005 ml) is placed on such a strip 1·5 cm from the lower edge, and the lower end of the strip is immersed to a depth of $\simeq$ 2 mm in 0·02N-HCl. The HCl rises up the paper strip, and causes an even diffusion of the Fe^{3+}, thus producing a pale-blue spot, the area of which is proportional to the concn. of Fe. With very dilute soln. the Fe is first concentrated, with simultaneous removal of any other ions present. The method can be used to determine $\nless$ 0·1 μg of Fe^{3+} per ml with an error $\ngtr$ 3%.
C. D. Kopkin

1539. **Spectrographic method for the quantitative determination of iron in veined quartz.** L. D. Svirskiĭ and V. L. Zhebunov. *Trudy̆ Khar'kovsk. Politekh. Inst.*, 1959, **31** (1), 147–151; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,093.—*Procedure*—Place the sample (15 mg), ground in a copper mortar, in a cavity (diam. 3 mm, depth 2·8 mm) in a carbon electrode, and excite the spectra in an arc discharge at 8 amp. with a carbon upper electrode. Evaporate the sample for 7 min. Photograph the spectra in the large spectrograph KS-55. The analysis is carried out by the photometric interpolation method from the lines Fe 3020·6 and Si 3019·97 A. Prepare standards from rock crystal by adding $(NH_4)_2SO_4.FeSO_4.6H_2O$, in the concn. range 0·0005 to 1·0%. The kinetics of the evaporation of Fe is studied. The coeff. of variation of the determination is 9·5%. Grinding the samples in an agate mortar causes contamination with iron.
C. D. Kopkin

1540. **Photometric determination of iron as ferric azide.** K. Kapitańczyk, Z. Kurzawa and Z. Pryminski (Dept. Gen. Chem., Inst. Technol., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 413–417.—The red ferric azide complex is stable and shows maximum extinction at pH 4·5 to 5·5, provided that sufficient NaN_3 is present (0·5 g per 100 ml). At higher pH a turbidity due to basic ferric azide and $Fe(OH)_3$ develops, and mineral acid completely bleaches the colour at pH 4 or less. Copper in excess of 2 mg per litre interferes by forming an olive-coloured complex, and, owing to their colour, Ni, Co and Cr can be tolerated only up to 50 mg per litre. Salts of Bi, Sn, Ti and Pb hydrolyse at pH 4·5 to 5·5, and tartrates, citrates, phosphates and fluorides decolorise the red complex; Cl^-, NO_3^- and SO_4^{2-} do not interfere. Erratic results are obtained if Fe^{2+} are oxidised with H_2O_2, but conc. HNO_3 is a suitable oxidant. The method can be used over the range 0·02 to 2 mg of Fe^{3+} per 100 ml, and the sensitivity and accuracy are nearly equal to those of the thiocyanate method.
P. Brych

1541. **Determination of metal ions by means of TAA [thioacetamide] and EDTA. III. Determination of iron.** G. C. Krijn, A. S. Koster and G. den Boef (Lab. for Anal. Chem., Univ., Amsterdam, Netherlands). *Anal. Chim. Acta*, 1960, **23** (3), 240–245 (in English).—Iron (0·15 to 5 mg) can be determined in the presence of metals of group 2 and group 3. The group-2 metals are pptd. with thioacetamide in HCl soln. and filtered off. EDTA (disodium salt) is added to the filtrate, which is buffered to pH 11, $CaCl_2$ is added as demasking agent and the pptd. hydroxides of Al, Fe and Mn are filtered off. The Fe in the ppt. can be determined by the spectrophotometric method of Schneider and Janko (*Anal. Abstr.*, 1957, **4**, 1544); Co, Ni and Zn remain in soln. The test soln. containing 0·15 to 5 mg of Fe is made slightly acid with conc. HCl in a centrifuge tube and 4 drops of 6% aq. thioacetamide soln. are added. The tube is heated in a water bath for 15 to 30 min. to coagulate the ppt. and the soln. is filtered through a G4 sintered glass filter into a second centrifuge tube. This tube is heated again in the water bath to destroy the excess of thioacetamide, and cooled. Bromine water is added to oxidise the Fe to Fe^{III} and the excess is removed by heating. The soln. is neutralised with 20% aq. KOH soln. and 1 ml of 0·1M-EDTA (disodium salt) is added. The soln. is cooled and buffered to pH 11 with aq. NH_3 - NH_4Cl soln. and 1 ml of 0·3M-$CaCl_2$ is added to precipitate the Fe (with Al and Mn if present). The ppt. is coagulated by heating at 95°, centrifuged and washed; it is then dissolved in a little conc. HCl and transferred to a 100-ml flask; 8 to 10 ml of 0·1M-EDTA (disodium salt) is added, followed by 3 ml of 25% aq. NH_3 and 3 ml of 30% aq. H_2O_2. The soln. is diluted to vol. with water and the extinction of the Fe^{III} - EDTA -H_2O_2 complex is measured at 525 mμ. The colour is sensitive to light and the flask should be kept in the dark except when actually measuring the extinction. H. M.

1542. **Stylometric determination of sulphur in certain types of steel and welds.** A. S. Dem'yanchuk. *Avtomat. Svarka*, 1959, (12), 82–84; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,122.—The spectra are excited in a condensed spark discharge from generator IG-2 in a complex circuit (current, 3 amp.; capacity, 0·01 μF; inductance, zero; secondary gap, 3 mm; analytical gap, 2 mm). The electrodes are rods of spectrally pure carbon (10 mm diam.) with hemispherical ends. Sulphur is determined on stylometer ST-7, with sparking for 20 to 30 sec., from the lines S 5453·8 and N 5462·62 A. For convenience of photometry, the N line is positioned in the frame so that the edge of the frame is completely covered by the line Fe 5455·61 A, while the S line is outside the frame. A calibration curve of Δl *vs.* log C is constructed. The lower limit for the determination of S is 0·08%; the mean error is ± 4·6%. The determination of S in pyrites is carried out from the lines S 5639·9 and N 5666·6 A in the concn. range of 40 to 50% with an analytical gap of 1 mm. The S line is positioned within the frame while the N line remains outside it. The electrodes are rods of electrolytic copper shaped at the working end to a cylinder of diam. 1·8 mm. The standards are chemically analysed samples. A determination takes 3 to 5 min. The error is ± 3%. C. D. Kopkin

1543. **Photometric determination of chromium in steel and aluminium alloys.** W. D. Nordling (Grinnell Corp., Providence, R.I., U.S.A.). *Chemist Analyst*, 1960, **49** (3), 78–79, 88.—For the determination of Cr in steel, the sample soln. in H_2SO_4 is treated with ascorbic acid to reduce Fe^{III}, and the Cr is caused to react for 30 min. with EDTA (disodium salt) at 100°. The extinction is measured at 538 mμ. The pH must be 0·6 to 0·8. Cobalt ($\not>$ 20%), W and Mo do not interfere. For Cr in aluminium alloys, the sample is dissolved in 30% fluoroboric acid, which does not attack Cu. After filtration of the residue containing the Cu, ascorbic acid and H_2SO_4 are added and the procedure for steel is followed. P. D. Parr-Richard

1544. **Macro- and micro-determination of traces of cobalt. V. Analysis of 18-8 steel by activation with thermal neutrons.** D. Monnier, W. Haerdi and J. Vogel (Lab. de Chim. Minérale, Univ., Genève). *Helv. Chim. Acta*, 1960, **43** (3), 675–686 (in French).—The determination is carried out by means of the γ-radiation from ^{60}Co after irradiation of the sample for 15 hr. in a flux of $\simeq 10^{13}$ neutrons per sq. cm per sec. Iron interferes, and is removed by ion exchange. For this purpose the irradiated sample is dissolved in aqua regia and the HNO_3 is removed by repeated evaporation to dryness with HCl. The residue is then dissolved in 9M-HCl (100 ml) and an aliquot (1 ml) is diluted with 9M-HCl (10 ml) and passed through a column of Dowex 1-X8; Ni and Cr pass through and Co and Fe are retained, the Co being then eluted with 4M-HCl. For the γ-spectrometry, three procedures are described. (*i*)—After calibration of the instrument with a known standard of ^{60}Co, the height of the ^{60}Co peak for the sample is measured and substituted in an activation formula. For this procedure the conditions of irradiation must be precisely known. (*ii*)—A known amount of a cobalt salt is irradiated side by side with the sample, and the Co in the sample is determined by calculation from the corresponding peak heights. (*iii*)—The ^{58}Co formed from the Ni or Cr in the sample is used as an internal standard. For this procedure the content of Ni or Cr of the sample must be known. The sensitivity, precision, advantages and disadvantages of each method are discussed.

VII. Determination of micro amounts of cobalt in steel by polarography, spectrophotometry and neutron activation. Comparative study. J. Vogel, D. Monnier and W. Haerdi. *Ibid.*, 1960, **43** (5), 1254–1267 (in French).—The three methods are compared. Each requires the preliminary isolation of the Co. This is carried out by preferential adsorption on a Dowex I-X8 column, followed by elution with 4M-HCl. The soln. (after removal of acid) may be polarographed (*i*) with the addition of a further known amount of Co. The spectrophotometric method (*ii*) is based on measurement of the extinction at 520 mμ of the nitroso-R salt complex. (*iii*) The Co may be made radioactive by neutron bombardment of the sample (5 to 15 hr. at 10^{13} neutrons per sq. cm per sec.). and isolated as described before. The γ-ray spectrum may now be used for the determination of Co (*a*) with an internal standard (*i.e.*, a known quantity of Co is added and irradiated) (this is the recommended procedure); (*b*) with a prior calibration, *i.e.*, an external standard (not recommended); or (*c*) with ^{58}Co from the accompanying Ni as internal standard (useful for alloys of known nickel contents). The

sensitivity and precision decrease in the order (*ii*), (*iii*), (*i*); for ensuring freedom from interfering materials, all methods are much the same; for simplicity, γ-spectrometry is best; for speed (*i*) and (*ii*) are best. R. E. E.

J. L. PROSSER

1545. **New redox systems. III. Indirect cerimetric determination of cobalt.** F. Vydra and R. Přibil (Chem. Inst., Czech. Acad. Sci., Prague). *Talanta*, 1960, **5** (2), 92–96 (in English).—Bivalent cobalt may be determined by oxidation with Fe^{III} in the presence of 1,10-phenanthroline (**I**) (*Ibid.*, 1959, **3**, 103; 1960, **5**, 44) followed by the visual or potentiometric titration of the ferroin formed with standard $Ce(SO_4)_2$ soln. *Procedure*—Dissolve the sample (0·5 g) in aqua regia. Dilute, filter and wash the residue with dil. HCl. Neutralise an aliquot of the filtrate with 5% NaOH soln. until a ppt. forms, then add sufficient dil. HCl to re-dissolve it. Adjust the pH to between 2 and 4, add 0·1M-**I** (10 ml) and set aside for 15 min. Add 9N-H_2SO_4 (50 ml), dilute to 200 ml with water and titrate potentiometrically with 0·05M- or 0·1M-$Ce(SO_4)_2$ with platinum and saturated calomel electrodes; Fe^{3+} must be added if the sample contains less Fe than Co. Up to 2·9 mg of Co can be determined with an error $\not>$ 1% in the presence of Ni (110 mg), Cd (25 mg), Zn (65 mg), Cu (20 mg), Mo (30 mg), V (45 mg), Fe (90 mg) and W (50 mg); Ag, Hg and Th must be absent. W. T. CARTER

1546. **Co-precipitation of cobalt with tetrammino-nickel and [tetrammino]copper picrates.** P. A. Ganichev, I. N. Berezina and A. I. Glotova. *Trudў Khim. i Khim. Tekhnol.*, 1959, (1), 90–93; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 72,971.—The isotope ^{60}Co is used. The soln. (1 ml, containing 1000 μg of Ni^2 or Cu^{2+} and 10 μg of Co^{2+}) is placed in a centrifuge tube, and 1·5 ml of a 1% soln. of picric acid (**I**) in 1% aq. NH_3 (for Ni) or 4% aq. NH_3 (for Cu) is added. After 15 min. and testing for completion of pptn., the ppt. is centrifuged off, washed ($\times$ 2) with **I** soln., dissolved in 0·5 to 0·7 ml of HNO_3 (1:1), and the amount of co-pptd. Co determined. As the concn. of aq. NH_3 used to prepare the **I** soln. increases from 0·5 to 15%, the co-pptn. of Co with tetramminonickel picrate increases from 57 to 90% and, with tetramminocopper picrate, from 1 to 6%. At high concn. of aq. NH_3 practically complete co-pptn. of Co is achieved with the nickel salt. At a concn. of 0·1%, the Co in the sample does not interfere in the determination of Cu. From the study of the influence of the time of contact of the ppt. with the mother liquor, the temp., the amount of Co in the sample and other factors on the co-pptn., it is concluded that the co-pptn. of Co with these picrates is an adsorption process. C. D. KOPKIN

1547. **Determination of cobalt in metals and silicates by amperometric titration with potassium ferricyanide.** I. Bozsai (Iron and Metal Works, Csepel, Hungary). *Magyar Kém. Lapja*, 1960, **15** (9), 423–425.—The application of the conventional method to steel, tool steel, magnet steel, non-ferrous alloys, metallic nickel, electrical resistance materials (Kanthal), stellite, widia [tungsten carbide] and enamels is described; Fe^{3+}, Ni^{2+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, ClO_4^-, MoO_4^{2-} and VO_3^- do not interfere; Mn interferes, and a correction is necessary. The error is $\simeq \pm$ 0·1 mg of Co.

B. VASZKO

1548. **Separation of radio-cobalt from nickel.** R. Mills and M. J. Vernon (Res. School of Phys. Sci., Australian Nat. Univ., Canberra). *Anal. Chim. Acta*, 1960, **23** (4), 388–390 (in English).—The classical cobaltinitrite separation gives > 99% recovery of 5 mg of Co from 10 g of Ni with a standing time of 45 min. T. R. ANDREW

1549. **Precipitation of nickel dimethylglyoximate from homogeneous solution.** E. D. Salesin and L. Gordon (Case Inst. of Technol., Cleveland, Ohio, U.S.A.). *Talanta*, 1960, **5** (2), 81–85 (in English).—Dimethylglyoxime is generated in the presence of Ni by causing diacetyl to react with hydroxylamine at pH 7·5. The soln. is set aside at room temp. for $\not<$ 1 hr. and then heated to 80° to 90° for 2 hr. The ppt. consists of large, readily collected needle-like crystals; up to 200 mg of Ni may be handled. In the presence of Cu and Co the separation is superior to that obtained by conventional pptn., but low results for Ni are obtained in the presence of Co and Fe together, unless the standing time at room temp. is increased to 24 hr.

W. T. CARTER

1550. **Determination of nickel.** P. Spacu and I. Albescu (Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (1), 85–90.—The methods proposed are based on the formation of a complex of Ni with proguanil. *Gravimetric procedure*—A soln. containing 5 to 20 mg of Ni, diluted to 100 ml, is treated with excess of aq. NH_3 to form $[Ni(NH_3)_6]^{2+}$, then a 2% soln. of proguanil hydrochloride is added. Pptn. takes place in the cold at a pH of 9 to 10. After 1 hr. the ppt. is collected in an IG4 filter, then washed with boiling water, and aq. ethanol, and dried at 110°. The error on 0·14 to 1·5 mg is < 5%. *Spectrophotometric procedure*—The pptd. complex is dissolved in warm ethanol and the extinction is determined at 430 mμ. The method was used on amounts ranging from 15 to 200 μg and the error varied from − 3·4 to + 2·6%. Details are given for a procedure in the presence of Al, Zn, Fe and Mg. H. SHER

1551. **Analysis of high-purity nickel by use of the carbonyl process for concentrating traces of impurities.** D. M. Shvarts. *Zavod. Lab.*, 1960, **26** (8), 966–971.—The Ni in a 5-g sample is volatilised as $Ni(CO)_4$ and the residue is analysed spectrographically for Bi, Cd, Sn, Sb, Pb, Zn, As, Mn, Cu and Co. The method is suitable for determining contents of $\simeq 10^{-7}$ to 10^{-5}%. Special apparatus is described. G. S. SMITH

1552. **Spectrographic determination of magnesium in cathode nickel.** W. Bykowski and J. Trawiński (Rosa Luxemburg Electric Lamp Works, Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (3), 361–367.—The procedure is based on the method of Nielsch (*Metallkunde*, 1952, **43**, 370); a Fuessner condensed spark is used, with conc. HNO_3 as sample solvent. The carrier electrode is impregnated with 3% polystyrene in benzene. Copper, Fe, Mn and Si (< 0·2%) do not interfere. P. BRYCH

1553. **Fluorimetric determination of ruthenium.** H. Veening and W. W. Brandt (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1426–1428.—Bivalent Ru (0·3 to 2 μg) is determined as the complex with 5-methyl-1,10-phenanthroline (**I**) in the presence of Os ($\not>$ 25 μg) and of other platinum metals. Results are accurate to within ± 2%. The insol. complex of Pd with **I** has to be removed by centrifuging; Fe^{III}, Ce^{IV},

Mn^{II}, MnO_4^-, Ag and $Cr_2O_7^{2-}$ interfere. *Procedure*—To the platinum-metals soln., free from strong oxidising agents and from Fe, add 0·1% **I** soln. (15 ml), 20% NaCl soln. (20 ml) and 10% hydroxyammonium chloride soln. (5 ml) and adjust the pH to 6·0 with 5M-NaOH or HCl. Heat the soln. under reflux for 3 hr., then measure the fluorescence intensity in a 1-cm cell at 578 mμ. Determine the Ru content by comparison with a calibration curve. J. P. STERN

1554. **Rapid determination of rhodium.** I. Dema and V. Voicu (Inst. Atom. Phys., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (2), 323–328.—The proposed method is based on the production of the complex $[Rh(NO_2)_6][Co(NH_3)_6]$. *Procedure*—The neutral or slightly acid soln. containing 0·01 to 0·1 g of Rh per 100 ml is heated until almost boiling, then treated with excess of solid $NaNO_2$ till the colour changes from red to yellow, followed by dropwise addition of a warm satd. soln. of $[Co(NH_3)_6](NO_3)_3$ until the colour changes to orange. The mixture is cooled; the fine yellow cryst. ppt. is collected in an IG4 crucible, washed with 4 to 5 ml of abs. ethanol and 2 to 4 times with ether, and dried in a vacuum desiccator for 10 to 15 min. The error is $\not> \pm$ 1·0%. Bivalent Pd, Pb^{4+}, Os^{4+}, Fe^{3+}, Ni^{2+} and Cu^{2+} do not interfere; Ir^{3+} and Co^{2+} interfere; Ru must be removed before the determination. H. SHER

1555. **Thiourea complexes of some noble metals. A polarographic determination of rhodium.** F. Pantani and P. G. Desideri (Inst. of Anal Chem., Univ. Florence, Italy). *Talanta*, 1960, **5** (2), 69–74 (in English).—The thiourea complex of Rh^{III} gives a polarographic wave at $E_{\frac{1}{2}} = \simeq -0{\cdot}40$ V *vs.* the S.C.E. The supporting electrolyte is 0·5M in KCl and 0·2M in thiourea, and the soln. is heated for 10 min. on a boiling-water bath before analysis to stabilise the complex. Gelatin is added as a maximum suppressor and reproducible results are obtained in neutral or slightly acid soln. containing no SO_4^{2-} or NO_3^-. Platinum interferes, but an 8-fold excess of Ir over Rh has no effect; Pd gives a separate wave not due to a thiourea complex, and it is possible to determine Pd and Rh simultaneously with an accuracy of ≃ 3%. W. T. CARTER

1556. **Analytical chemistry of palladium. I. Gravimetric determination of palladium as di-iodo-complexes.** V. Voicu and I. Dema (Inst. Atom. Phys., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (2), 301–310.—Three new methods are proposed, based on the production of complexes with KI and pyridine, aniline or quinoline of the form (PdX_2I_2), where X is the base. (*i*) *Procedure with pyridine*—The slightly acid soln. containing 0·01 to 0·1 g of $PdCl_2$ is treated dropwise with pyridine until decolorised, and then with 0·01 to 1 g of KI. The yellow cryst. ppt. is collected after 5 to 10 min. in an IG3 or 4 crucible, and washed with a mixture of 0·05 to 1 g of KI and 2 to 5 drops of pyridine diluted to 100 ml. The ppt. is suction-dried, washed with 3 to 4 ml of abs. ethanol, then 2 to 3 times with ether, and dried for 10 to 12 min. in a vacuum desiccator. The error is $\not> \pm$ 0·25% on 0·04 g. (*ii*) *Procedure with aniline*—The dil. acid (0·01N to 0·05N-HCl) soln. of 0·01 to 0·1 g of $PdCl_2$ is boiled, then treated with an excess of a 30% ethanolic soln. of aniline until the soln. turns pale yellow, followed by 0·01 to 0·1 g of KI. The soln. is cooled and the yellow-orange ppt. is treated as described above, the wash liquid containing 0·05 to 0·1 g of KI per 100 ml of water. The error is $\not>$ 0·25% on 0·04 g. (*iii*) *Procedure with quinoline*—The boiling soln. (as in the procedure with aniline) is treated with a 30% ethanolic soln. of quinoline until the soln. is faintly yellow, and then with 0·01 to 0·1 g of KI. The yellow-orange ppt. is treated as described above. The error is $\not>$ 2·0% on 0·16 g. Iridium and Rh do not interfere, but $[PtCl_6]^{2-}$, Os, Fe, Cu and Cd interfere. It is claimed that the method requires only 30 to 40 min.

II. Gravimetric determination of palladium as thiocyanato-complexes. I. Dema and V. Voicu. *Ibid.*, 1960, **8** (2), 311–316.—The two methods proposed are based on the production of complexes with pyridine or quinoline of the form $[PdX_2(SCN)_2]$. *Procedure with pyridine*—Pyridine is added until the soln. (50 to 70 ml, containing 0·01 to 0·05 g of Pd) is decolorised, followed by 0·1 g of NH_4SCN. The yellow pearly ppt. settles in 5 to 10 min., is collected in an IG4 filter and washed with a soln. containing 2 to 3 drops of pyridine and 0·06 to 0·1 g of NH_4SCN in 100 ml of water. The ppt. is suction-dried, washed with 1 to 2 ml of abs. ethanol and once or twice with ether, and vacuum-dried. *Procedure with quinoline*—To the sample soln. heated to 50° to 60° are added 15 to 20 ml of 50% ethanol, a 50% ethanolic soln. of quinoline until the soln. turns slightly yellow, and 0·1 g of NH_4SCN. The mixture is stirred until a yellow-orange cryst. ppt. settles. This is cooled, and collected as described above but washed with a 0·08% aq. soln. of NH_4SCN, then suction-dried, and washed with 3 to 5 ml of abs. ethanol and 2 to 3 times with ether and vacuum-dried. The error in each procedure is $\not>$ 1·0%.

III. Gravimetric determination of palladium with pyridine and potassium dichromate. V. Voicu and I. Dema. *Ibid.*, 1960, **8** (2), 317–321.—The proposed method is based on the production of $[PdPy_4][Cr_2O_7]$. In the absence of Rh^{3+}, Ni^{2+}, Co^{2+} and Mn^{2+}, 50 ml of the soln. containing 0·005 to 0·05 g of Pd at pH 4 to 6·5 is boiled and treated with pyridine until the yellow-orange colour is discharged, and then with an excess of a satd. soln. of $K_2Cr_2O_7$ until the mixture is yellow. After cooling the soln., the yellow cryst. ppt. is collected in an IG3 or 4 crucible, and washed first with 2 to 4 ml of a satd. soln. of $K_2Cr_2O_7$ plus 0·5 ml of pyridine in 100 ml of water, then 3 to 5 times with 1 ml of abs. ethanol and 2 to 3 times with ether, and dried in a vacuum desiccator for 10 to 15 min. The error is $\not> \pm$ 1·5%. In the presence of Rh^{3+}, Ni^{2+}, Co^{2+} or Mn^{2+}, the soln. treated with pyridine is further treated with ≃ 0·1 g of EDTA and heated on a water bath for 10 to 15 min., after which $K_2Cr_2O_7$ is added as described above. The error is $\not> \pm$ 2%. Bivalent Cu, Cd^{2+} and $[PtCl_6]^{2-}$ interfere. H. SHER

1557. **Colorimetric determination of palladium in uranium fission element alloys.** L. E. Ross, G. Kesser and E. T. Kucera (Chem. Engng Div., Argonne Nat. Lab., Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1367–1368.—*Procedure*—To the sample soln. (30 ml, containing 5 to 25 μg of Pd) in a 60-ml separating-funnel add EDTA (disodium salt) soln. (3%) (2 ml), adjust the pH to 1·0 to 2·0, add 1-nitroso-2-naphthol soln. (1%) (0·1 ml), set aside for 10 min. and extract with 10 ml of toluene. Wash the toluene extract with N-NaOH (10 ml) and centrifuge the organic layer to remove droplets. Measure the extinction of the toluene layer at 370 mμ. T. R. ANDREW

1558. **Photometric determination of palladium in the products of nickel production.** S. E. Kreimer, L. P. Butÿlkin and A. V. Stogova ("Severonickel" Combine, U.S.S.R.). *Zhur. Anal. Khim.*, **1960**, **15** (4), 467–471.—It is shown that an exchange reaction takes place between soln. of palladium dimethylglyoximate (**I**) in $CHCl_3$ and aq. di-antipyrinylmethane (**II**) and aq. KI soln. with the probable formation of the complex $(C_{23}H_{24}O_2N_4)_2.H_2[PdI_4]$. Add aqua regia (30 ml) to nickel tailings (0·5 g), heat the mixture and evaporate almost to dryness; treat the residue twice with conc. HCl and again evaporate. Add H_2O to the residue, filter off the insol. portion, wash it with hot H_2O, and ignite it with the filter-paper; fuse the residue with $K_2S_2O_7$ and extract the melt with H_2O. Add this soln. to the main soln. and reduce the vol. to 100 ml by evaporation. Add conc. HCl (3 ml) and 1% ethanolic dimethylglyoxime soln. (10 ml), stir vigorously and set the mixture aside for 15 min. Extract with $CHCl_3$ (10 and 5 ml), combine the extracts and wash them with 0·2N-HCl (2 or 3 × 25 ml). Add 40% KI soln. (10 ml) and 2% **II** soln. (20 ml) in 0·5N-HCl and shake for 2 min. Run off the $CHCl_3$ layer, add $CHCl_3$ (2 ml) to the remaining soln., shake vigorously and run off the $CHCl_3$ layer. Combine the extracts, wash them as before and dilute them to 25 ml with $CHCl_3$. The cherry-red colour is measured against a standard at 450 mμ. For an alternative photometric determination of Pd, evaporate the $CHCl_3$ soln. of **I** to dryness on a water bath, decompose **I** by heating with aqua regia (25 ml), evaporate to dryness, add conc. HCl (10 ml) and evaporate almost to dryness. Dissolve the chlorides by heating with H_2O, add 0·1% nitroso-R-salt soln. (10 ml), heat to boiling, cool, and dilute the soln. to 100 ml. Measure the extinction with a green filter. This method is suitable for the determination of Pd in tailings from nickel production containing $\not>$ 45% of Ni, $\not>$ 20% of Cu, and $\not>$ 5% of Fe. The method is modified for products containing a comparatively large amount of Fe. K. R. Cook

1559. **Spectrophotometric determination of palladium with o-mercaptobenzoic acid.** I. Dema and V. Voicu (Inst. Atom. Phys., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, **1960**, **8** (1), 173–178.—A soln. of the sample in 50% acetone at a pH between 2 and 4 containing < 2·6 μg of Pd per ml is treated with 5 drops of an ethanolic soln. of *o*-mercaptobenzoic acid. The max. extinction is at 428 mμ. There is no interference from Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Cd^{2+}, Al^{3+}, Au^{3+}, Rh^{3+} (< 1:2), TeO_4^{2-} or Au^+, but Pt^{4+}, Pt^{2+}, Rh^{3+} (> 1:2), Cr^{3+} (in large amounts), I^- and oxidising agents interfere. H. Sher

1560. **Separation of palladium from niobium and zirconium.** J. F. Duke and W. Stawpert (Nat. Phys. Lab., Teddington, Middx., England). *Analyst*, **1960**, **85**, 671–672.—The method is based on the ability of Pd to form a complex iodide, PdI_4^-, whereas neither Nb nor Zr forms a stable iodide in aq. soln., and the extraction of this iodide into isobutyl methyl ketone. Alloys of Pd and Zr are dissolved in aqua regia and fumed with H_2SO_4. Alloys of Pd and Nb are fused with $KHSO_4$ and the residue is dissolved in oxalic acid. Sulphuric acid and KI are then added, the KI to an excess of 10% over that required to precipitate the palladous iodide. A vol. of isobutyl methyl ketone equal to that of the aq. phase is added and the mixture is shaken intermittently until the colour of the aq. layer is discharged. The separated organic layer is back-washed with a little H_2SO_4 (20%), and the separation of Pd from Nb and Zr is then complete. After removal of solvent and destruction of organic matter with HNO_3, the Pd is determined gravimetrically with dimethylglyoxime. The Nb and Zr in the aq. layer are determined by pptn. with cupferron and subsequent ignition to the oxides. A. O. Jones

1561. **Organic reagents for osmium.** G. Baiulescu, C. Lazar and C. Cristescu (Parhon Univ., Bucharest). *Zhur. Anal. Khim.*, 1960, **15** (4), 505–506.—4-Acetamidobenzaldehyde thiosemicarbazone (**I**) is used as a 0·1% soln. in 1% NaOH soln. and 4-nitrobenzaldehyde thiosemicarbazone (**II**) is used as a 0·05% soln. in 1% NaOH soln. An H_2SO_4 soln. (conc. H_2SO_4 - H_2O) (8:17) (1 ml) is added to 0·1 to 3·0 ml of the osmium soln., then **I** or **II** soln. (2 ml) is added and the mixture is set aside, for 5 min. with **I** and for 15 min. with **II**; each soln. is then diluted to 10 ml with ethanol. A yellow - brown colour is obtained with **I** and a red - brown colour with **II**. The max. extinction in both cases is measured at 436 mμ in a Pulfrich photometer. The use of **I** and **II** enables 1·2 to 14·7 μg of Os per ml and 0·49 to 8·60 μg of Os per ml, respectively, to be determined. These reagents are more sensitive than thiourea. K. R. Cook

1562. **Neutron activation analysis for iridium in platinum.** L. S. Jowanovitz, F. B. McNatt, R. E. McCarley and D. S. Martin, jun. (Inst. for Atomic Res., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1270–1272.—The sample, after irradiation, is dissolved in aqua regia and Ir is then pptd. as the hydroxide and counted with a scintillation spectrometer. Hydrated IrO_2 is used as an external standard; the use of ^{195m}Pt as an internal standard is not recommended. The coeff. of variation reported for a 0·04-p.p.m. sample (7 replicates) is 10%. K. A. Proctor

1563. **Spectrographic determination of impurities in iridium and rhodium.** A. A. Kuranov, V. D. Ponomareva and N. I. Chentsova. *Zhur. Anal. Khim.*, **1960**, **15** (4), 476–480.—It is shown that reference standards for spectrographic analysis of iridium and rhodium can be prepared from metal powders. A method is described for the determination of Pt, Au, Pd, Ru, Fe, Ni, Al, Cu, Si, Pb, Ba and Rh in iridium and the first 11 elements and Ir in rhodium. Graphite powder (0·05 g) is added to each of three 0·1-g portions of metal powder (iridium or rhodium), each mixture is ground carefully and then compressed in a steel matrix (diam. 4 mm) under pressure (4000 to 5000 kg per sq. cm). A spectrograph with a triple-lens system, a slit width of 0·017 mm for the analysis of iridium and 0·025 mm for rhodium, a lower rod-shaped graphite electrode (diam. 6 mm) with a truncated conical tip, an electrode gap of 2·5 mm and an a.c. arc with an 8-amp. current as an excitation - activation source, are used. The exposure time is 60 sec. All standards and samples are photographed three times through a three-stage attenuator. Type-I spectrographic plates are used for the long-wave region and type-II plates for the short-wave region. K. R. Cook

1564. **Determination of free acid in the presence of hydrolysable cations.** A. Moscowitz, J. Dasher and H. W. Jamison, jun. (Crucible Steel Co. of America, Pittsburgh, Pa.). *Anal. Chem.*, **1960**, **32**

(10), 1362–1364.—A simple method is given for the determination of free acid in the liquors resulting from the pickling of stainless-, silicon-, alloy- and carbon-steels and of titanium with HNO_3, H_2SO_4 and HNO_3 - HF, and in similar soln. In favourable cases, the error is $< \pm 2\%$. *Procedure*—Dilute to 50 ml an aliquot containing 1 to 10 milli-equiv. of free acid. If the sample is an iron-pickling liquor, add 11·6% $Fe(NO_3)_3.9H_2O$ soln. (0·2 ml). If the sample does not contain HF, add also 32% NH_4F soln. (0·6 ml). If the sample is a titanium-pickling liquor, add $Fe(NO_3)_3$ soln. (2 ml) and NH_4F soln. (0·6 ml). Titrate with 0·2N-NaOH to the first visible red - brown ppt.; the soln. turns yellowish just before the end-point.

A. R. ROGERS

1565. **Analysis of small samples of monazites with a gamma scintillation spectrometer.** G. H. M. Couwenberg, C. L. D. Kooy and A. E. Korvezee (Lab. of Phys. Chem., Tech. Univ., Delft, Holland). *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (8), 895–909 (in English).—The γ-ray spectra of a number of specimens of known radioactive-element content have been examined and the information is used to determine the U and Th contents of monazites. The results obtained for low U contents are not as good as with chemical analysis. In leached ores, where the radioactive equilibrium with Ra, etc., has been disturbed, the results are only approximate.

E. J. H. BIRCH

1566. **Determination of arsenic in coal and coke.** S. R. Crook and S. Wald (Nat. Coal Board, Scientific Dept., Albert Embankment, London). *Fuel, London*, 1960, **39** (4), 313–322.—Methods for the determination of As in anthracite have been examined in several laboratories during the revision of BS 1016. In the method adopted, the ground sample is mixed with MgO and $KMnO_4$ and burned in O. The As is extracted with acid and reduced to AsH_3, which is then absorbed and oxidised by means of iodine soln. The intensity of the molybdenum blue colour developed by the addition of ammonium molybdate and hydrazine sulphate is measured and the As is determined by reference to a calibration curve. Repeatability and reproducibility are both 1·0 p.p.m. of As_2O_3 for samples containing $<$ 6 p.p.m., and 1·5 p.p.m. for samples with $>$ 6 p.p.m. The method is also applicable to coal and coke and can be used for the simultaneous determination of P. The paper-stain finish, although less precise, is also to be retained in BS 1016.

G. BURGER

1567. **Free cyanide analysis of copper cyanide plating solutions.** J. R. Crain (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Plating*, 1960, **47** (9), 1032–1035.—For the most accurate value of "free" cyanide, the cold method is recommended; the ice must be weighed out accurately since $[CN]^-$ is affected by changes in dilution. Whilst the rate at which the "free" cyanide content is increased, by dissociation of $[Cu(CN)_3]^{2-}$, is negligible at the temp. of the cold method (3° to 5°), this effect is increasingly important at higher temp. and causes high results. The end-point is more difficult to detect at higher temp. and the increased titration time could also introduce errors.

J. H. WATON

See also Abstracts—**1341**, Determination of gases in metals. **1346**, Indicator for mercurimetry of halides. **1350**, Pptn. of Cu - Sn group with H_2S. **1351**, **1352**, Ion exchange for qual. separation of metals. **1661**, Determination of K in presence of NH_4^+. **1642**, Fe, Ni and V in petroleum. **1663**, Metallochromic indicator for Ca. **1733**, **1734**, Be in air. **1739**, Be in natural water. **1775**, Apparatus for determination of hydrazine in soln. **1776**, O in titanium and steel.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather and explosives.

1568. **Preliminary examination of organic compounds yielding water and ammonia by spot-test analysis.** F. Feigl and J. R. Amaral (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1960, (5–6), 816–820 (in German).—The detection of 8 classes of compound that yield NH_3 or H_2O on pyrolysis is described. By heating these at 120° to 180° with thiobarbituric acid (**I**) or Michler's thioketone, H_2S is liberated. *Procedure*—Add a little solid **I** and 1 to 2 drops of ethanol or benzene to a drop of test soln. in a micro test-tube. Evaporate to dryness and place the tube with a piece of Pb acetate paper over the open end in a glycerol bath at 110°. Heat gradually to 180°; a positive reaction is indicated by the appearance of a black or brown stain in a few minutes. The limit of detectability is 0·3 to 50 μg. A test with hexamine and Nessler reagent for compounds yielding water only is also described.

P. D. PARR-RICHARD

1569. **Infra-red analysis, alone and combined with other techniques, as a tool in the determination of the structure of organic compounds.** C. la Lau (Koninkl. Shell Lab., Amsterdam, Netherlands). *Chem. Weekbl.*, 1960, **56** (39), 537–541.—Examples are given of the use of i.r. spectrophotometry, alone and in combination with u.v. spectrophotometry, Raman spectroscopy and mass spectrometry.

M. J. MAURICE

1570. **The formation of active complexes in the oxidation layer during elementary analysis.** G. Kainz and H. Horwatitsch (Anal. Inst. der Univ. Wien, Austria). *Mikrochim. Acta*, 1960, (5–6), 917–926 (in German).—Several compounds were submitted to combustion over CuO at different temp. under N and the amount of CO_2 formed was measured. Ease of oxidation was in the order CO, acetic acid, acetylene, petroleum, ethylene, benzoic acid, xylene, toluene, benzene and methane. Except for homologues, the b.p. was no criterion of ease of oxidation. With petroleum, a step-wise reaction occurred, because of the intermediate formation of methane; the acids behaved similarly, though CO_2 was rapidly formed from the carboxyl group. Combustion of acetylene and ethylene was incomplete. Oxidation occurs by the formation of cleavage products which are successively adsorbed and desorbed by CuO until oxidation is complete; methane has the lowest retention time and thus resists oxidation most strongly. The influence of various factors on oxidative efficiency is discussed.

P. D. PARR-RICHARD

1571. **Conductimetric micro-determination of carbon and hydrogen in organic compounds.** N. E. Gel'man and Ven-Yun Van (Inst. of Organic Elements and Compounds, Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 487–494.—After pyrolytic combustion of the organic sample in a rapid stream of O, the H_2O obtained is frozen with a mixture of solid CO_2 and acetone, and the CO_2 obtained is passed into an electroconductivity cell in which it is absorbed by dil. NaOH or $Ca(OH)_2$ soln. The frozen H_2O is evaporated in a stream of Ar or N on to a layer of hot platinised carbon black, the CO formed is then oxidised over heated CuO, and the resulting CO_2 is passed into an electroconductivity cell containing a dil. soln. of alkali. The C and H are measured by the change in conductivity of the absorbing soln. The reproducibility of results is more satisfactory than with the gravimetric method and, except for weighing the sample, the entire procedure can be made fully automatic. It can be used for the determination of solids and liquids containing N, halogens (including F), S, B, Si, P and metals. Recoveries for a number of organic substances are tabulated.
K. R. Cook

1572. **Simultaneous micro-determination of carbon, hydrogen and halide.** A. S. Zabrodina and N. F. Egorova. *Vestn. Moskov. Univ., Ser. Khim.*, 1960, II, No. 4, 66–70.—Metallic copper at a temperature of 10° to 15° quant. absorbs Br and Cl. A Cl-containing compound, when burnt in a stream of O, produces a significant amount of HCl; CuO is therefore mixed with the metallic copper to react with the HCl to form H_2O, which is absorbed on anhydrone before and after the combustion products are passed over the copper - CuO mixture. Hydrogen bromide is not produced in significant amounts when Br-containing compounds are burnt. The accuracy of the determination for C and H is within $\pm$ 0·2% and for halides within $\pm$ 0·4%.
A. Burwood-Smith

1573. **Sodium dispersions in elementary analysis.** J. Patrick and F. Schneider (C.W. Post College, Brookville, N.Y., U.S.A.). *Mikrochim. Acta*, 1960, (5–6), 970–972 (in English).—The conventional fusion method for detecting N, halogens, S, etc., in organic compounds is modified by using a dispersion of sodium in toluene; this serves not only to decompose the sample but to reduce any N to NH_3. *Procedure*—Place 1 μg to 1 mg of substance into a capillary tube sealed at one end and add 5 to 10 times as much of the dispersion. Place a piece of red litmus paper over the open end and warm the tube. To identify S, destroy the excess of sodium with ethanol, transfer the soln. to a clean tube and acidify with HNO_3. Detect H_2S with Pb acetate paper. P. D. Parr-Richard

1574. **Automatic chloride analyser.** D. M. Coulson and L. A. Cavanagh (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1245–1247.—A completely automatic method for the coulometric titration of I^-, Br^- and Cl^- in combustible samples is described. Small samples (0·5 to 1 mg) can be analysed in 10 min. with an accuracy greater than that by other methods. K. A. Proctor

1575. **Micro-determination of nitrogen based on the Dumas method. Improvements in the Shelberg and Schöniger technique.** R. Lévy and B. Cousin (Centre Nat. de la Rech. Sci., 39 bis rue de Dantzig, Paris). *Mikrochim. Acta*, 1960, (5–6), 854–862 (in French).—Modifications to Schöniger's apparatus (*Mikrochem.*, 1952, **39**, 229) are described and illustrated. These consist of a simplified gas-flow path, a readily replaceable packing, more flexible connections and movable electric furnaces which can be opened. The method of use, described in detail, gave good precision with, for example, tryptophan, and certain systematic errors have been eliminated. P. D. Parr-Richard

1576. **Ultra-micro determination of nitrogen in samples of organic substances weighing not more than 0·5 mg.** G. Gutbier and M. Boëtius (Tech. Hochschule, Dresden, Germany). *Mikrochim. Acta*, 1960, (5–6), 636–640 (in German).—The determination of N in 0·1 to 0·5-mg samples is possible by the Dumas method with a miniature Pregl apparatus. A CO_2 regulator is incorporated to permit reproducible blanks to be obtained. Errors are from + 0·3 to − 0·1%. J. P. Stern

1577. **Determination of small amounts of nitrogen in organic material. Elimination of traces of nitrogen from reagents and protection therefrom during the analysis.** H. Roth (Agric. Exp. Sta., B.A.S.F., Limburgerhof, Germany). *Mikrochim. Acta*, 1960, (5–6), 663–669 (in German).—The N ($\simeq$ 10 p.p.m.) is determined by the Kjeldahl technique and measured photometrically by means of Nessler reagent in an ELKO II photometer with a S42 filter. For such small amounts of N, large samples (1 to 2 g) are required; also, blanks must be kept low and constant both by purification (described) of reagents and by excluding atmospheric basic N compounds by means of a water-filled U-tube. By this means blanks equiv. to 4 to 6 μg of N are reproducibly attained with 20 ml of soln. The need for repeated blank determinations is thus eliminated; alternatively, the photometric reading is taken against a blank determination and the blank value thus eliminated.
J. P. Stern

1578. **Rapid volumetric micro-determination of phosphorus in organic substances.** R. Püschel and H. Wittmann (Univ., Graz, Austria). *Mikrochim. Acta*, 1960, (5–6), 670–674 (in German).—The Schöniger combustion method is followed by direct cerimetry (with 0·005M-Ce^{3+}) of the PO_4^{3-} produced, with Eriochrome black T (**I**) as indicator. Errors are < 0·3% of P and maximum deviations of duplicate determinations on 3-mg samples are within $\pm$ 0·2%; F, As, Si or metals forming complexes with **I** interfere. J. P. Stern

1579. **Application of the flask combustion method to the micro-determination of phosphorus in organic substances.** A. Dirscherl and F. Erne (F. Hoffmann-La Roche and Co. A.-G., Basel, Switzerland). *Mikrochim. Acta*, 1960, (5–6), 775–788 (in German).—Loss of P in the Schöniger combustion procedure is ascribed to its retention in carbon deposited on the platinum gauze, and is avoided by the use of a larger flask and by the addition of $(NH_4)_2S_2O_8$ to the sample. J. P. Stern

1580. **Simultaneous determination of traces of selenium and mercury in organic compounds by X-ray fluorescence.** E. C. Olson and J. W. Shell (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (3), 219–224 (in English).—Solid samples (600 mg) are weighed into a special aluminium plate, having a depression in which the

sample is compressed into a block with the aid of a hydraulic press. Liquid samples are irradiated in an aluminium cell with a Mylar window. Irradiation is with a tungsten-target X-ray tube operated at 50 kV and 45 mA. A lithium fluoride analysing crystal and a Tl-activated sodium iodide scintillation counter are used. The intensity of the L_α line at 36·00° 2θ is used for the determination of Hg and the K_α line at 31·88° 2θ for Se. The intensity of the L_β line of W is also measured, and the ratios of the intensities of the Se and Hg lines, respectively, to the W line are calculated. The values found are compared with a calibration graph prepared from standard samples treated in a similar manner. The intensities are found by measuring the time required for 10^6 counts. The method is claimed to give results accurate to $\pm$ 1 p.p.m. for samples containing 2 to 40 p.p.m. of Se or Hg.

H. M.

1581. **Qualitative functional-group analysis of gas-chromatographic effluents.** J. T. Walsh and C. Merritt, jun. (Pioneering Res. Div., Quartermaster Res. and Engng Centre, U.S. Army, Natick, Mass.). *Anal. Chem.*, 1960, **32** (11), 1378–1381.—A method of qual. gas-chromatographic analysis is described in which retention-time data are combined with functional-group colorimetric tests. The method is rapid and simple, and requires little extra time and no expensive supplementary instrumentation. The technique can also be used to decide whether a chromatographic peak consists of one or more components.

C. B. BAINES

1582. **Acetyl-group determination using acetic anhydride labelled with carbon-14.** R. H. Benson and R. B. Turner (Radioisotope Res. Lab., Veterans Admin. Hospital, Houston, Texas, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1464–1465.—The sample is acetylated in pyridine by heating with labelled acetic anhydride (prep. described) (2 millimoles per expected hydroxyl group for 1 millimole of sample) at 125° for 4 hr. The product is poured into H_2O and ethyl ether is added. The ether layer is extracted successively with dil. HCl, dil. NaOH soln., H_2O and satd. NaCl soln. After evaporation of the ether, the product is purified by chromatography and recrystallisation. Alternatively, the acetylation can be carried out in the presence of labelled Na acetate as a catalyst instead of in pyridine. A weighed amount of the derivative is dissolved in dimethylformamide, and the specific activity is determined in a flow counter. The number of acetyl groups is obtained by dividing by two the value obtained for the specific activity of the acetic anhydride.

G. BURGER

1583. **Infra-red absorption spectrum of methane from 2470 to 3200 cm^{-1}.** E. K. Plyler, E. D. Tidwell and L. R. Blaine (Nat. Bur. Stand., Washington, D.C.). *J. Res. Nat. Bur. Stand., A*, 1960, **64** (3), 191–212.—A total of 2460 lines were measured in this region. The observed spectrum is shown in five charts.

1584. **Gas - solid chromatographic separation of some light hydrocarbons.** T. A. McKenna, jun., and J. A. Idleman (Firestone Synthetic Rubber and Latex Co., Orange, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1299–1301.—Separate the saturated and ethylenic hydrocarbons up to C_4 by passage successively through a 10-ft. column of 60 to 80-mesh silica (Davison Grade 62, previously heated at 310° for 1 hr.) and a 10-ft. column of 60 to 80-mesh alumina (Alcoa Grade F-10, previously heated overnight at 110°), at a temp. in the range 30° to 90°, with He as carrier gas at 150 ml per min. Before use, the columns must be purged with He until all water is eluted (up to 24 hr.). Alternatively, use a 30-ft. column, containing 20·8% of propylene carbonate on alumina, at room temp.

A. R. ROGERS

1585. **Hydrogenation as an aid in the identification of unsaturated hydrocarbons by gas chromatography.** B. Smith and R. Ohlson (Inst. f. Organisk Kemi, Chalmers Tekn. Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1960, **14** (6), 1317–1324.—Methods are described for the complete hydrogenation of unsaturated hydrocarbons and the stepwise hydrogenation of alkadienes and of alkynes in fractions from gas-chromatographic analyses. These are particularly useful in the identification of dienes and alkynes, and also permit the detection of unsaturated hydrocarbons in specific chromatographic bands and the conversion of unseparable unsaturated hydrocarbon mixtures into separable saturated mixtures, *e.g.*, mixtures of 3- and 4-methylpentene were hydrogenated to 3- and 2-methylpentane and subsequently separated on squalane.

S. M. MARSH

1586. **Determination of chloroform in aqueous solution.** E. A. Robinson (A. R. Davis & Co. Ltd., Croydon, Surrey, England). *Anal. Chim. Acta*, 1960, **23** (4), 305–308 (in English).—The hydrolysis of $CHCl_3$ by aq. soln. of alkali has been studied as a function of alkali concn. for NaOH and KOH.

T. R. ANDREW

1587. **Rapid determination of 3-chloropropene by methoxymercuration.** K. L. Mallik (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1369–1370.—To 0·05M- or 0·1M-3-chloropropene in methanol add an excess of 0·1M-mercuric acetate in methanol, 0·005M to 0·01M in $HClO_4$, set aside at room temp. for 15 min. and titrate with 0·1N-HCl in butanol, with diphenylcarbazone as indicator. Perform a blank determination. The recoveries in four replicate assays ranged from 99·1 to 100·5%.

A. R. ROGERS

1588. **Quantitative determination of ethylene epoxide [epoxyethane], propylene epoxide [1,2-epoxypropane] and higher-molecular-weight epoxides using dodecanethiol.** B. J. Gudzinowicz (Petrochem. Dept., Nat. Res. Corp., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1520–1522.—A procedure is described for the determination of epoxides in mixtures to which other methods cannot be applied. The sample, in aq. or organic soln., is shaken with a standard soln. of dodecanethiol in ethanol and an amount of ethanolic KOH soln. slightly in excess of that required to neutralise the sample (separately determined). After 20 min., acetic acid and isopropyl alcohol are added, and the excess of the thiol is titrated with iodine soln. The values found are more accurate than those obtained with the $MgCl_2$ - HCl procedure, but less so than those given by the $HClO_4$ - $NaIO_4$ method (*cf.* Eastham and Latremouille, *Canad. J. Res., B*, 1950, **28**, 264). High concn. of aldehydes interfere.

G. BURGER

1589. **Determination of C_3- and C_4-alcohols in benzene.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1960, **32** (10),

1372.—Infra-red data are given for n-propanol, s-butyl alcohol, isopropyl alcohol and t-butyl alcohol in benzene.

1590. **Gas - liquid chromatography of allylic alcohols and related branched-chain acids.** G. Popják and R. H. Cornforth (Hammersmith Hospital, Ducane Road, London, W.12). *J. Chromatography*, 1960, **4** (3), 214–221.—The relative retention volumes (R_v) of polyprenols (compounds containing isoprenoid units) and related branched-chain acids are reported. Two columns were used, one containing ethanediol - adipic acid polyester on Celite and one containing Apiezon L on Celite. All determinations were made at 197° with a 120 cm × 4 mm column and a gas-density balance. Identification is reasonably certain when values of R_v for both columns are used. The separation factors (ratios of R_v) for compounds differing by specific groups or configurations (*e.g.*, isoprenoid unit or *trans - cis*) are tabulated. R. M. S. Hall

1591. **The catalytic spot-test detection of ether.** F. Feigl, R. J. Amaral and D. Haguenauer-Castro (Lab. da Prod. Mineral, Min. Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1960, (5–6), 821–826 (in German).—By rapid evaporation of pure ethyl ether in air and heating at 200°, ether peroxide is formed, which catalyses the oxidation of Cu acetate - benzidine reagent. Other solvents, *e.g.*, benzene, toluene and CS_2, prevent this reaction, but such interference is masked by the addition of a small amount of $CHCl_3$ or CCl_4. Certain other aliphatic ethers give a positive reaction, but cyclic ethers do not. *Procedure*—Place a drop of ether in a micro-test-tube and cover the open end with a paper impregnated with a 1:1 mixture of aq. saturated soln. of Cu acetate and benzidine chloride. Immerse in a glycerol bath at 200°; a blue colour appears after about 1 min. P. D. Parr-Richard

1592. **Determination of chloride ion in ethanediol by pCl measurement.** R. B. LeBlanc and R. T. McFadden (Texas Div., Dow Chem. Co., Freeport, U.S.A.). *Talanta*, 1960, **5** (2), 78–80 (in English).—Up to 1 p.p.m. of Cl^- in ethanediol can be determined with silver - silver chloride and satd. calomel electrodes separated by a KNO_3 salt bridge. The conductivity of the sample (100 ml) is increased by the addition of 3M-KNO_3 (5 drops) and the cell potential is measured with a pH meter that has previously been standardised with samples of known Cl^- content. Propionaldehyde (30 p.p.m.), acetic acid (10 p.p.m.) and Fe (0·5 p.p.m.) are without effect, but 1 p.p.m. of Fe gives an error of − 0·1 p.p.m. of Cl^-. The sensitivity is 0·1 p.p.m. and the accuracy ± 0·1 p.p.m. W. T. Carter

1593. **Evaluation of crude glycerin.** L. V. Cocks (Unilever Ltd., Res. Dept., Port Sunlight, Ches., England). *Analyst*, 1960, **85**, 686–687.—The method of evaluating glycerin by means of the "organic residue," which is the total residue at 160° less the ash, is a tedious analytical process and the result gives no indication of the presence of impurities volatile at 160°. The value of the so-called "matter-(organic)-non-glycerol" (MONG) figure, which is 100 less the sum of the glycerol (by the KIO_4 method), ash and water (by the Karl Fischer method), has been examined and 418 sets of figures have been collected to compare MONG with "organic residue." In quoted examples where MONG is higher than the "organic residue" the difference is shown to be due to the presence of propane-1,3-diol. It is concluded that, in normal crude glycerins, MONG is a figure of the same order as the "organic residue," while in abnormal crude glycerins MONG includes organic impurities (volatile at 160°) that would not be included in the "organic residue" figure, and it is proposed that MONG should be considered as an improved alternative to "organic residue." A. O. Jones

1594. **Colour reactions given by sugars and diphenylamine - aniline spray reagents on paper chromatograms.** R. W. Bailey and E. J. Bourne (Royal Holloway Coll., Englefield Green, Surrey, England). *J. Chromatography*, 1960, **4** (3), 206–213.—The use of the spray reagent of Buchan and Savage (*Analyst*, 1952, **77**, 401) has been extended. Specific colours are given with uronic acids, aldoheptoses and methylpentoses when heated at 80° (5 min.). Specific reactions with pentoses at 60° are not affected by the first two groups of compounds. When the diphenylamine and aniline are successively sprayed, dried and heated instead of being applied as a mixture, specific colour reactions are given with all aldohexoses and reducing aldohexose disaccharides not containing a 1,4 link and also with some ketoses. D-Fructose (red - brown) and L-sorbose (yellow) are clearly differentiated, while furfuraldehyde and 5-hydroxymethylfurfural are not. The substitution of triphenylamine for diphenylamine did not yield useful results. R. M. S. Hall

1595. **Sugar determination according to Luff - Schoorl.** E. L. Krugers Dagneaux and P. Raymond (Lab. N.V.P. de Gruyter en Zn., 's-Hertogenbosch, Netherlands). *Chem. Weekbl.*, 1960, **56** (38), 533–534.—A modification is proposed of the Luff - Schoorl procedure (*Ibid.*, 1929, **26**, 132). The reaction mixture is now kept at 120° for exactly 10 min. A new table is given for lactose. For other sugars the Luff - Schoorl tables can be used. M. J. Maurice

1596. **Qualitative micro-determination of carbonyl compounds by radial chromatography of their hydrazones.** L. Peyron (Antoine Chiris, Grasse, France). *France et ses Parfums*, 1959, **2** (12), 41–48.—Functional carbonyl groups in plant extracts were blocked as acylhydrazones, transformed into coloured arylhydrazones, and identified by radial chromatography. One part of the plant material was mixed with 10 parts of cold carbonyl-free dichloromethane for 10 min. The filtrate from this was heated under reflux for 3 hr. with Girard's reagent D (*NN*-dimethylglycine hydrazide hydrochloride) (25 mg per g of extract), and the cooled soln. was mixed with an equal vol. of H_2O and decanted. A second extraction with an equal vol. of benzene removed all H_2O-insol. fractions. The aq. layer was shaken for 3 hr. with a soln. of dinitrophenylhydrazine equiv. to the wt. of reagent D, 2 ml of conc. HCl, 5 ml of ethanol, 15 ml of dichloromethane and 10 ml of H_2O. After being decanted, the solvent layer was washed with H_2O, dried over Na_2SO_4, and concentrated to 5 ml. The dinitrophenylhydrazones were roughly separated on a column of activated alumina with benzene and ethanol, and the yellow and orange fractions were concentrated to 2 ml and radially chromatographed in 5 ml of dimethylformamide, 4 ml of cyclohexane and 2 ml of cyclohexene. Chem. Abstr.

1597. **Study of the catalytic oxidation of propene. III. Methods for determining acraldehyde in the catalytic oxidation products of propene over a copper catalyst.** V. P. Latÿshev and N. I. Popova. *Izv. Sibirsk. Otd. Akad. Nauk SSSR*, 1959, (9), 48–51; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,226.—The bromide - bromate and spectrophotometric methods and the polarographic method of Kirillova and Korshunov (*Brit. Abstr. C*, 1952, 12) for determining acraldehyde (**I**) are compared. The bromide - bromate method is unsuitable; the spectrophotometric method gives low results in the presence of polymers of **I**; the polarographic method gives accurate results for the determination of **I** in all possible mixtures of the oxidation products of propene if 0·1N-HCl is used as basal electrolyte. Propionaldehyde, glyceraldehyde, acetaldehyde and pyruvaldehyde do not interfere. (*Cf.* Popova and Vermel', *Anal. Abstr.*, 1959, **6**, 599.) C. D. Kopkin

1598. **Analysis of 1,2-glycols and polyhydric compounds. V. Determination of glyceraldehyde by means of the formaldehyde liberated with periodate.** L. Maros, I. Molnár-Perl and E. Schulek (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **24** (1), 67–71 (in German).—The test soln. is set aside for 1 hr. with periodic acid soln. in a glass-stoppered conical flask. A slight excess of 1·5M-aq. Na_2SO_3 is added and the soln. is neutralised with 10% aq. acetic acid. A small excess of acid is added and the flask is closed and shaken. Pentane (5 ml) is added and the flask is set aside for 30 min.; a little starch soln. is added and the soln. is made alkaline with 20% NaOH soln.; 0·2 to 0·3 g of KCN is added and dissolved by swirling and after 2 to 3 min. the soln. is made slightly acid with HCl, and the liberated H_2SO_3 is titrated with 0·1N-iodine. An accuracy of ± 0·5% is claimed. The direct determination of glyceraldehyde with $NaHSO_3$ and standard iodine soln. is also described. H. M.

1599. **Determination of acetals, ketals and vinyl ethers.** B. Budešínský and J. Körbl (Res. Inst. f. Pharm. and Biochem., Prague, Czechoslovakia). *Mikrochim. Acta*, 1960, (5–6), 697–702 (in German). —These substances are simultaneously hydrolysed and oximated in 30 min. at 100° by a soln. 1M in HBr and 0·1M in hydroxyammonium chloride. After cooling, the soln. is treated with 10M-KOH, and the excess of hydroxylamine is titrated potentiometrically with $K_3Fe(CN)_6$ soln. after 30 min. The potential at the end-point is ≃ − 200 mV. The accuracy on 20 to 150 mg is within ± 1·25%. J. P. Stern

1600. **Combined detecting reagent for the identification of organic acids on paper chromatograms.** J. Pásková and V. Munk (Central Res. Inst. of Food Indust., Prague-Smichov, Czechoslovakia). *J. Chromatography*, 1960, **4** (3), 241–243.—The reagent consists of (*i*) a soln. containing 0·075% of bromocresol green and 0·025% of bromophenol blue in abs. ethanol and (*ii*) an aq. soln. containing 0·5% of $KMnO_4$ and 1% of $Na_2CO_3.10H_2O$. Equal volumes of (*i*) and (*ii*) are mixed and sprayed immediately. The mixed soln. is unstable after 10 min. Colours are tabulated for 18 common organic acids and enable identifications to be made of acids having similar R_F values; n-butanol - formic acid - water (10 : 1 : 5) is a suitable solvent. R. M. S. Hall

1601. **Simplified chromatographic separation and analysis of C4 through C12 dibasic acids.** E. D. Smith (The Chemstrand Corp., Decatur, Ala., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1301–1304.—*Procedure*—Mix coarse dry silicic acid (prep. described) (25 g) with water or M-citrate buffer of the appropriate pH (16 ml) and pack with suction in a column (40 cm × 2 cm). Add the sample (≃ 50 mg) dissolved in $CHCl_3$ (10 ml) or in a 10% soln. of 2-methylbutan-2-ol in $CHCl_3$ (10 ml) and develop at a flow rate of 2 ml per min., by application of pressure of N, with $CHCl_3$ followed by successive mixtures of $CHCl_3$ and n-butanol containing increasing concn. of butanol up to 40%. As stationary phases use H_2O to separate the C_4 to C_7 acids, buffer of pH 5·40 for the C_7 to C_{10} acids, and buffer of pH 7·8 for the C_9 to C_{12} acids. Analyse the 10-ml fractions of eluate gravimetrically by evaporation and weighing. A precision of ± 5% is achieved. A. R. Rogers

1602. **Micro-determination of chloro-substituted acetic acids.** F. Gölles (Inst. Pharmacognosy, Univ. Graz, Austria). *Mikrochim. Acta*, 1960, (4), 597–606 (in German).—The method of Fischer and Kartnig (*Anal. Abstr.*, 1961, **8**, 1287) is applied to the rapid micro-determination of the three chloroacetic acids with phenol (critical mixing temp. 65·5°). Mixture-gap diagrams are given and confirm the agreement of the max. temp. with those found on the Kofler block. The only other liquid suitable for use with all three chloroacetic acids is *m*-cresol (critical mixing temp. of 150°). J. P. Stern

1603. **Determination of anhydrides of carboxylic acids by means of hexamethyleneimine and piperidine.** A. P. Terent'ev, S. I. Obtemperanskaya, M. M. Buzlanova and T. E. Vlasova. *Vestn. Moskov. Univ., Ser. Khim.*, 1960, II, No. 4, 71–73.—The method is based on the reaction of anhydrides with secondary amines and permits their determination in the presence of acid with an accuracy of ± 0·25%. *Procedure*—Place 0·05 g of anhydride in a 100-ml flask with a ground-glass stopper and add hexamethyleneimine or piperidine (0·1N in dioxan) (10 ml). After 5 min. add 5 drops of indicator, prepared by mixing 40 ml of 0·1% ethanolic methyl red, 10 ml of 0·1% ethanolic methylene blue, 50 ml of ethanol and 100 ml of water) and titrate with 0·1N-HCl in methanol to a colour change from green to pink. A. Burwood-Smith

1604. **Kinetic approach to the identification of aliphatic amines.** T. Aung, E. A. Healy and R. K. Murmann (Univ. of Missouri, Columbia, U.S.A.). *Chemist Analyst*, 1960, **49** (3), 73.—A primary aliphatic amine in the presence of H_2O, alcohols or secondary amines may be identified by measurement of the first-order dissociation in acid soln. of the complex between Fe^{II} and the Schiff base formed by the amine with picolinaldehyde (**I**). *Procedure*—To 0·1 ml of faintly acid soln. (≃ 0·2M in amine) add 0·1 ml of methanol and 1 drop of **I** - methanol soln. (1 : 3). Add 1 to 2 drops of 10% $FeCl_2$ soln. and shake. After 5 min. transfer 1 to 3 drops to 3 ml of 0·1 or 0·25M-HCl (adjusted with NaCl to an ionic strength of 1). Measure the change in extinction with time at a controlled temp.; the half-time (obtained from the graph of log extinction *vs.* time) is characteristic for each amine. Small amounts of aromatic amines do not interfere. P. D. Parr-Richard

1605. **Chromatography of organic substances. VII. Determination of aliphatic amines by gas chromatography.** J. Franc and M. Wurst (Forschungsinst. f. Org. Synthesen, Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (9), 2290–2295 (in German).—The amines are separated on a column of kieselguhr or Celite with a stationary phase of Elastomer E 301 (Griffin and George); N is used as the carrier gas and the operating temp. is 23°. Volatile amines are first converted into hydrochlorides. The separated amines are burned in a combustion apparatus, the H_2O formed being then converted into H over heated iron, and then determined by means of a thermal-conductivity cell. Relative elution times are given for 20 amines. The coeff. of variation for a single compound is $\pm$ 1·4% (100 determinations). G. P. Cook

1606. **Analysis of hydroxamic acids and hydrazides: preparation and properties of dinitrophenyl derivatives of hydroxamic acids, oximes, hydrazides and hydrazones.** S. Seifter, P. M. Gallop, S. Michaels and E. Meilman (Albert Einstein Coll. of Med., Yeshiva Univ., New York 61, U.S.A.). *J. Biol. Chem.*, 1960, **235** (9), 2613–2618.—Three methods are given for the determination of hydroxamic acids. The first is a modification of Hill's method (*Brit. Abstr. C*, 1948, 257) and is used when the excess of hydroxylamine has been removed by dialysis or extraction. The hydroxamic acid soln. is mixed with $Fe(ClO_4)_3$ soln. in 50% ethanol and the extinction is measured at 505 mμ. When hydroxylamine is present, the method of Lipmann and Tuttle (*Brit. Abstr. C*, 1945, 276) is used. The second method is based on that of Bergmann and Segal (*Anal. Abstr.*, 1956, **3**, 2122), which depends on the oxidation of hydroxamic acids by iodine to give nitrous acid, which is then used to diazotise sulphanilic acid. The resulting diazonium compound is coupled with 1-naphthylamine, and the extinction is measured at 520 mμ. The third method depends on the reaction of free hydroxylamine with indole to give a yellow compound, the extinction of which is measured at 400 mμ. In this method a preliminary hydrolysis of hydroxamic acid is needed to yield free hydroxylamine. Amidoximes may also be determined by any of these methods. When precautions are taken to ensure the removal of all free hydroxylamine before the determination, the iodine-oxidation and indole methods are much more sensitive than the $Fe(ClO_4)_3$ method. An extremely sensitive method is given for the determination of hydrazides with *p*-dimethylaminobenzaldehyde. J. N. Ashley

1607. **Differentiation of some diazines.** B. Berisso (Univ. Nac. del Litoral, Rosario, Argentina). *Mikrochim. Acta*, 1960, (5–6), 898–901 (in Spanish).—The use of a 2% molybdophosphoric acid soln. for the identification and differentiation of piperazine, pyrazine, pyridazine and pyrimidine by means of the characters of the microcrystalline ppt. formed is described. N. E.

1608. **Amperometric titration of EDTA and DCyTA.** D. Roubalova and J. Doležal (Pedagogic High School, Charles' Univ., Prague, Czechoslovakia). *Chemist Analyst*, 1960, **49** (3), 76.—EDTA and DCyTA (1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid) (**I**) soln. can be titrated amperometrically with $Hg(NO_3)_2$ soln. in a mixture of 0·2M-Na acetate and 0·2M-acetic acid at pH 5 to 6, and an applied potential of 0·1 V; fuchsine is used as a max. suppressor. The average error was 0·2%. Determination of Hg^{II} by titration with EDTA or **I** was also successful. P. D. Parr-Richard

1609. **Analysis of sulphonic acids and salts by gas chromatography of volatile derivatives.** J. J. Kirkland (Ind. and Biochem. Dept., Exp. Sta., E.I. du Pont de Nemours and Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1388–1393.—The quant. conversion of the acids and salts into volatile derivatives, and the subsequent analysis, with thermistor detectors, are described. Aliphatic, aromatic and alkylarylsulphonic acids and their salts are converted into their corresponding sulphonyl chlorides by the use of thionyl chloride or phosgene in the presence of a formamide derivative as a catalyst. Free sulphonic acids are converted into their corresponding methyl esters by the use of diazomethane, the preparation of which is described. Recoveries of 96 to 100% are attained for all reactions carried out by the recommended procedures. C. B. Baines

1610. **New colorimetric applications of the chromate - o-dianisidine system. II. Indirect colorimetric determination of some mercapto-compounds: thioglycollic acid, thiolactic [2-mercaptopropionic] acid and thiomalic [mercaptosuccinic] acid.** F. Buscaróns, J. Artigas and C. Rodriguez-Roda (Fac. of Sci., Univ., Barcelona, Spain). *Anal. Chim. Acta*, 1960, **23** (3), 217–218 (in English).—The compounds named are treated with an excess of K_2CrO_4 and the excess is determined by measuring the red colour produced when the K_2CrO_4 reacts with *o*-dianisidine in acid soln. *Procedure*—Potassium chromate soln. (200 μg per ml) (2 ml) is transferred to a 100-ml flask and the test soln. is added from a micro-burette, in an inert atmosphere to avoid oxidation of the mercapto-compounds; 2 to 3 ml of 5N-H_2SO_4 is added and the soln. is set aside for 5 to 10 min. *o*-Dianisidine soln. (0·5 g dissolved in 50 ml of acetone and diluted to 100 ml with water) (0·5 ml) is added and the red colour is measured at 470 mμ, 5 to 25 min. later. Results are referred to the appropriate calibration curve. Low concn. (0·1 to 5 μg per ml) can be determined. H. M.

1611. **Differential conductimetric titration of a mixture of methylchlorosilanes in non-aqueous solutions.** A. P. Kreshkov and V. A. Drozdov. *Dokl. Akad. Nauk SSSR*, 1960, **131** (6), 1345–1348; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,199.—The determination of di- and tri-component mixtures of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$ and CH_3SiCl_3 is based on the quant. conversion of the chlorosilanes into the alkylthiocyanato-derivatives by the action of NH_4SCN, and conductimetric titration in methyl cyanide - ethyl ether (2:3) with 0·1M-amidopyrine in benzene. The mono-substituted compound is first titrated, then the di-substituted, and finally the tri-substituted. The smallest amounts which can be determined in the mixture are, $(CH_3)_3SiCl$ 0·0055 g, $(CH_3)_2SiCl_2$ 0·0025 g, and CH_3SiCl_3 0·0023 g in 12 ml. Concentrated soln. must be diluted. The error in determining the individual chlorosilanes is $\pm$ 2%. C. D. Kopkin

1612. **Potentiometric titration of individual alkylchlorosilanes with organic bases in methyl cyanide.** A. P. Kreshkov, V. A. Drozdov and E. G. Vlasova. *Izv. Vȳssh. Ucheb. Zavedeniĭ, Khim. i Khim.*

Tekhnol., 1960, **3** (1), 85–87; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,200.—Titration in methyl cyanide with 0·05N-phenazone or nitron in methyl cyanide, or with a soln. of amidopyrine in benzene, by visual and potentiometric methods is suggested. The indicators used were crystal violet, dimethylaminoazobenzene, bromocresol purple, methyl orange, bromophenol blue and gallo sea blue (C.I. Mordant Blue 14); $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3 and $SiCl_4$ were titrated; the error of the determination is $\pm$ 0·3%. The addition of benzene, toluene, chlorobenzene or CCl_4 does not affect the results. A new cell is described for potentiometric titrations in non-aq. solvents of low dielectric constant. C. D. KOPKIN

1613. **Potentiometric titration of nitrogen-containing organosilicon compounds in non-aqueous media.** A. P. Kreshkov, V. A. Drozdov and E. G. Vlasova. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 80–84; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,203.—It is suggested that nitrogen-containing organosilicon compounds be titrated with $HClO_4$ soln. in methyl cyanide, methyl nitrite, or their mixtures with benzene or dioxan, by visual or potentiometric methods. The indicators used were crystal violet, bromocresol purple, bromophenol blue, cresol red, dimethylaminoazobenzene, thymol blue, methyl red and methyl orange. Compounds containing N attached directly to Si, and compounds with N in an organic radical, have been titrated. The potential jumps when titrating in methyl nitrite are 10 mV larger than those in methyl cyanide. The amount of titrating soln. used is proportional to the number of N atoms in the molecule of the compound. The error is $\not>$ 1·5%. C. D. KOPKIN

1614. **Analysis of dilute solutions of triethylaluminium [in petroleum spirit].** R. Z. Lioznova and M. L. Genusov (Okhtensk Chem. Combine). *Zavod. Lab.*, 1960, **26** (8), 945–947.—Apparatus for determining $(C_2H_5)_3Al$ from the volume of ethane liberated by the action of water is described. A correction is made for the solubility of ethane in the solvent. G. S. SMITH

1615. **Partition chromatography of aromatic hydrocarbons on rubber-like polymers.** G. L. Starobinets and E. V. Povarkov (Lenin Univ., Minsk, USSR). *Zhur. Anal. Khim.*, 1960, **15** (4), 405–408.—In this chromatographic method the carrier of the stationary phase is omitted and the components to be separated are distributed between the stationary high-molecular-weight phase [a vulcanisate of unfilled polymer SKB (sp. gr. 1·002) containing 2% of S] and a low-molecular-weight mobile phase (methanol - H_2O, containing from 24·6 to 37·2% by vol. of H_2O depending on the coeff. of distribution of the hydrocarbons between the polymer and the methanol - H_2O). Chromatography is carried out in a column of diameter 1·6 cm with a 26·4-cm layer of stationary phase. Part of the stationary phase is removed from the column and then the test mixture is introduced directly into the upper part of the stationary phase. After adsorption for 1 to 2 hr., the mobile solvent is passed through at the rate of 0·2 ml per min. A typical mixture separated contained benzene (0·1 ml), toluene (0·15 ml), *p*-xylene (0·2 ml) and mesitylene (0·1 ml). The amounts of these hydrocarbons recovered were, respectively, 0·105, 0·155, 0·21 and 0·1 ml. The mean error is $\not>$ 5%. K. R. COOK

1616. **Fluorescence spectra of aromatic hydrocarbons and heterocyclic aromatic compounds.** B. L. Van Duuren (Inst. of Ind. Med., New York Univ. Med. Centre, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1436–1442.—The application of fluorescence spectroscopy to the qual. and quant. analysis of aromatic compounds is described. The effects of concn., solvent and pH on fluorescence intensity are examined for a number of compounds of differing fluorescent properties. The effects of replacing hydrogen atoms of aromatic hydrocarbons by alkyl groups, and of carbon atoms by nitrogen and oxygen, are also examined. Results obtained augment identifications of compounds made on the basis of u.v. and fluorescence emission spectra. C. B. BAINES

1617. **Determination of benzene, toluene and xylene in their mixtures by gas - liquid chromatography.** D. A. Vyakhirev and M. I. Ostasheva. *Trudy Khim. i Khim. Tekhnol.*, 1959, (1), 128–132; *Ref. Zhur., Khim.*, 1960, (16), Abstr. No. 65,185.—The separation and determination of mixtures of benzene, toluene and xylene are carried out at 100° in a stream of N (80 ml per min.) on a column (100 cm long, 0·6 cm internal diam.) of diatomite containing 30% (w/w) of triethylene glycol. Results calculated from the peak heights were more accurate than those calculated from the peak areas. The errors are < 5%. K. R. COOK

1618. **Chromatographic determination of the content of heterocyclic sulphur compounds in commercial benzene and naphthalene.** M. Hřivnáč and J. Janák (Lab. Gas Analysis, Brno, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (8), 399–403.—The analysis was carried out in a Griffin and George apparatus, type MK II, with polyoxyalkylene adipate (Reoplex 400, Geigy) (30%) as stationary phase, on Celite 545 for thiophen separation (temp. 85°) or on Sterchamol (Dortmund) for thionaphthen separation (temp. 175°). Hydrogen was used as carrier gas. *Determination of thiophen in benzene by the standard addition method*—Place 40 to 100 µl of the sample on the column and chromatograph at 85°. Repeat the procedure with the same sample to which has been added 10 µg of thiophen per ml. *Determination of thionaphthen in technical naphthalene by the internal standard method*—Melt the sample (5 g), stir to homogenise and cool. Into a small test-tube weigh durene (1,2,4,5-tetramethylbenzene) (10 mg) and cover it with the test sample (1 g). Add $\simeq$ 5 drops of 1-methyl-naphthalene to decrease the m.p. Heat till just liquid, place 40 to 100 µl on the column and chromatograph at 175°. Samples containing > 0·05% of thiophen or > 0·1% of thionaphthen can be analysed within 40 min. with an accuracy of $\pm$ 10%. J. ZÝKA

1619. **Determination of ethylbenzenes.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1960, **32** (10), 1372.—Infrared data are given for ethylbenzene and the three diethylbenzenes.

1620. **Analysis of phenylalkanes by gas chromatography.** C. F. Spencer and J. F. Johnson (California Research Corp., Richmond, U.S.A.). *J. Chromatography*, 1960, **4** (3), 244–248.—Retention times are listed for the series phenylhexanes to phenyleicosanes and some n-paraffin reference compounds from n-decane to n-tetracosane with a 12-ft. asphalt - firebrick column at 240°, 270°

and 320°. Separation of some isomers is not always possible. Accuracies given for the determination of 1- to 6-phenyldodecane mixtures range from + 5 to − 8%. R. M. S. HALL

1621. **Gas - liquid chromatographic separation and analysis of chlorinated toluenes.** S. K. Freeman (Benzol Products Co., Newark, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1304–1306.—To separate and analyse a mixture of ring and side-chain Cl derivatives of toluene, use a 7-ft. column of 20% of silicone oil (Dow Corning No. 550) on firebrick (Burrell, Kromat-FB) at 170° in combination with a 7-ft. column of 20% of Ucon 2000 on firebrick at 170°, with He as carrier gas at a flow rate of 100 ml per min. Peak-area correction factors for a mixture of 7 components ranged from 0·73 to 1·55. A. R. ROGERS

1622. **Quantitative determination of the main impurities in technical cumene hydroperoxide by infra-red absorption spectra.** N. K. Rudnevskiĭ and V. V. Zharkov. *Trudy Khim. i Khim. Tekhnol.*, 1959, (1), 119–124; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,191.—A method is developed for the quant. determination of cumene hydroperoxide (**I**), dimethylphenylcarbinol (**II**) and acetophenone (**III**) in the products of the oxidation of cumene (**IV**), by their i.r. absorption spectra. **III** is determined independently of the content of the other components by measuring the extinction by the base-line method at 5·93 μ. **I** is also determined independently at 11·98 μ, on the assumption that the mixture of **I** and **IV** is a binary mixture, because of the low content of **II** and **III**. **II** is determined at 11·55 μ by the method of successive approximations, allowing for the concn. of **I**. The relative errors are, for **I**, ± 1·6% (concn. range 19 to 86%); for **II**, ± 5·5% (1 to 4%); and for **III**, ±5% (0·5 to 2·5%). C. D. KOPKIN

1623. **Analysis of multicomponent mixtures by infra-red absorption spectra. II. Determination of chlorocumene, t-butylchlorobenzene and chlorodiphenylmethane isomers.** Yu. Ya. Mikhaĭlenko, N. N. Lebedev, I. K. Kolchin and E. G. Kutÿrina (Mendeleev Chem.-Technol. Inst., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (4), 495–499.—Sylvite cells are used in the spectrophotometer with a path length of 0·09 cm, the method being that described previously (*Anal. Abstr.*, 1960, **7**, 5295). Suitable wavelengths for *o*-, *m*- and *p*-chlorocumene are 13·27, 12·77 and 12·11 μ, respectively; for *o*-, *m*- and *p*-t-butylchlorobenzene, 13·03, 12·75 and 12·10 μ, respectively; and for *o*-, *m*- and *p*-chlorodiphenylmethane, 13·35, 12·95 and 12·63 μ, respectively. Max. absorption occurs at 9·64 μ and at 9·09 μ. The extinction is measured in CS_2 soln. Determinations of synthetic mixtures of the compounds mentioned have a mean relative error of ≃ 4%. K. R. COOK

1624. **Determination of *o*-, *m*- and *p*-cresols from their infra-red absorption spectra.** N. A. Chumaevskiĭ (Inst. of Elemento-organic Compounds, Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (8), 957–959.—Contents are determined from measurements of absorption at 756, 778 and 816 cm^{-1}. G. S. SMITH

1625. **Spot-test detection and colorimetric determination of aliphatic aldehydes with 2-hydrazinobenzothiazole. Application to air pollution.** E. Sawicki and T. R. Hauser (Air Pollution Engng Res., Robert A. Taft Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1960, **32** (11), 1434–1436.—The test described is especially sensitive to formaldehyde. The sample of vapour or soln. is brought into contact with a soln. of 2-hydrazinobenzothiazole in HCl, and $K_3Fe(CN)_6$ soln. is added to give a brown colour, which changes to purple on addition of NaOH soln. and to an intense blue on subsequent addition of dimethylformamide. Procedures are described for spot tests on plates or paper and on silica gel contained in a tube, and for a colorimetric determination. Identification limits for formaldehyde, acetaldehyde and propionaldehyde are 0·01, 0·3 and 0·5 μg, respectively, but are much higher for other aliphatic aldehydes. Aromatic and heterocyclic aldehydes give negative results. High concn. of nitromethane interfere. G. BURGER

1626. **Determination of aromatic aldehydes by near-infra-red spectrophotometry.** R. M. Powers, J. L. Harper and Han Tai (A. E. Staley Mfg. Co., Decatur, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1287–1289.—The method described can be used to determine aromatic aldehydes in the presence of aromatic ketones. Of three characteristic absorption bands, the 2·21-μ region is used because it is relatively free from interference, the only interferences in this region being from terminal epoxides and cyclopropyl groups. K. A. PROCTOR

1627. **Mass spectra of aromatic esters.** E. M. Emery (Colgate-Palmolive Co., Jersey City, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1495–1506.—The mass spectra are listed of 25 aliphatic esters of aromatic acids and 17 aromatic esters of aliphatic acids. Characterisation of these esters is obtained from fragmentation patterns and the spectra can be used for the identification of unknown esters and the determination of esters in mixtures. Examples are given of several analyses of synthetic mixtures showing excellent results. C. B. BAINES

1628. **Non-aqueous titration of phenolic esters.** B. Smith and Å. Haglund (Inst. f. Organsk Kemi, Chalmers Tekn. Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1960, **14** (6), 1349–1352.—Potentiometric titration of phenolic esters with 0·1N-tetra-n-butylammonium hydroxide in benzene-methanol as titrant and acetone as solvent is a suitable method for differentiating between various types of ester. Results are tabulated for 27 phenolic esters. The esters of aliphatic carboxylic acids can be titrated provided that strongly electron-repelling groups are not present in the phenolic ring. Unsubstituted esters of aromatic carboxylic acids do not react, but the introduction of an electron-attracting group into the aromatic nucleus can make such esters reactive. The mechanism of the reaction is briefly discussed, together with some exceptions to the general rules. S. M. MARSH

1629. **Effect of substituent groupings on the chromatographic behaviour of phenoxyacetic acids. I. Methyl-substituted phenoxyacetic acids.** L. S. Bark and R. J. T. Graham (Roy. Tech. Coll., Salford, England). *Analyst*, 1960, **85**, 663–666.—An investigation by paper chromatography of a series of methyl-substituted phenoxyacetic acids suggested that the phenoxyacetate group plays a dominant part in the adsorption of the acids or their ammonium salts on material with which the carboxyl group can form hydrogen bonds, and is

therefore the fundamental group. To ensure that the variation in the R_F and R_M values of the series was produced only by changes in the chemical structure, the conditions were rigorously standardised. The solvents were n-butanol saturated with water and n-butanol saturated with aq. NH_3. The results suggest that, in addition to the fundamental group factors, there are, for these nuclear-substituted compounds, at least two factors dependent on the position of the steric group relative to the fundamental group, and on the position of the substituent groups relative to each other, and that the greater the distance between the fundamental group and the substituent group the smaller the effect on the R_M value of the molecule, and that the nearer the substituent groups are to one another the smaller is the effect on the R_M value.

A. O. JONES

1630. **Determination of aromatic primary amines and compounds containing reactive methylene groups by diazotisation and C-nitrosation reaction using alkyl nitrites.** N. K. Mathur, S. P. Rao and Dau Narain (Jaswant Coll., Jodhpur, India). *Anal. Chim. Acta*, 1960, **23** (4), 312–316 (in English).—Primary amines, acetylacetone and dimedone in HCl soln. (4N) may be titrated potentiometrically with alkyl nitrite soln. The temp. should be kept between 5° and 10°. T. R. ANDREW

1631. **Solvent and concentration effects on the near-infra-red N-H bands of primary aromatic amines.** K. B. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Div. of Eastman Kodak Co., Kingsport, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1281–1286.—The effects of change of concn. in the range 0·5 to 100% and change of solvent on the first overtone stretching and combination N–H bands of aniline, *m*-toluidine, *o*-chloroaniline and *m*-chloroaniline were determined in the solvents cyclohexane, CCl_4, CS_2, benzene, $CHCl_3$ and methyl cyanide. Quant. analysis in the overtone region can be made in 10-cm cells at concn. $<$ 0·1M in all solvents except cyclohexane, but only CCl_4, CS_2 and $CHCl_3$ can be used in the combination region. Deviations from Beer's law are serious in 1-cm cells at concn. between 0·1M and M in cyclohexane, CS_2 and CCl_4. An improvement in accuracy is possible by using integrated molar extinction coeff.

A. R. ROGERS

1632. **Ultra-violet spectrophotometric analysis of solutions of benzonitrile and benzamide.** M. J. Astle and J. B. Pierce (Case Inst. of Technol., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1322–1324.—The molar fractions of benzonitrile (**I**) and benzamide (**II**) in soln. in the presence of water and alcohols can be determined by measurement of the u.v. absorption at a single wavelength if the total number of moles of **I** and **II** is held constant, and the molar fraction is used as the unit of concn. A. R. ROGERS

1633. **[Infra-red] spectrometric analysis of the isomeric composition of mixtures of diamino- and di-isocyanato-toluenes.** A. I. Finkel'shteĭn and E. N. Boĭtsov. *Zavod. Lab.*, 1960, **26** (8), 959–963.—With nitromethane as solvent, 2,4- and 2,6-diaminotoluenes are determined from infra-red absorptions at 11·86, 12·57 and 12·87 μ, and 2,4- and 2,6-di-isocyanatotoluenes are determined from absorptions at 12·35 and 12·80 μ.

G. S. SMITH

1634. **Titanous chloride as a reagent for quantitative organic micro-analysis. II. Micro-determination of azo and diazonium compounds and of nitroarylhydrazines.** J. V. Earley and T. S. Ma (Chem. Dept., Brooklyn Coll., N.Y., U.S.A.). *Mikrochim. Acta*, 1960, (5–6), 685–692 (in English).—Azo and diazonium compounds and nitroarylhydrazines are determined in acetate buffer at room temp. by reaction with excess of $TiCl_3$ soln. and back-titration with $(NH_4)_2SO_4.Fe_2(SO_4)_3$. The accuracy on 4 to 8 mg of sample is within $\pm$ 0·2%. Titration with $TiCl_3$ in strong HCl permits the determination of many azo and nitroso compounds in the presence of many nitro compounds (*cf.* Ma and Earley, *Anal. Abstr.*, 1959, **6**, 3558).

J. P. STERN

1635. **A new spot-test reaction for various nitrobenzene derivatives.** V. Anger (Forschungslab. der Firma Loba Chemie, Wien XIX, Austria). *Mikrochim. Acta*, 1960, (5–6), 827–830 (in German).—Diphenylbenzidine (**I**) in 80% H_2SO_4 is oxidised by nitroso-compounds; certain aromatic nitro-compounds give a similar reaction after reduction with Devarda's alloy. Possible reaction mechanisms are discussed. *Procedure*—To the aq. or ethanolic soln. of the sample in a clean test-tube add 0·5 ml of **I** soln. (1 mg of **I** in 10 ml of 80% H_2SO_4) and 1 drop of reducing agent (10 mg of powdered alloy suspended in 10 ml of H_2O) and warm at 100°. A positive reaction is shown by the appearance of a blue colour after 1 to 5 min.; the limit of detection is 5 to 10 μg. It is possible to distinguish between, *e.g.*, *p*-chloronitrobenzene (positive reaction) and *o*-chloronitrobenzene (negative). Nitrobenzene and its homologues do not react.

P. D. PARR-RICHARD

1636. **Qualitative test for mononitrotoluenes with trisodium pentacaynoamminoferrate.** C. B. Hackett and R. M. Clark (Res. and Devel. Dept., Nobel Div., I.C.I. Ltd., Stevenston, Ayrshire, Gt. Britain). *Analyst*, 1960, **85**, 683–684.—A drop of the sample or 10 mg of the sample in hot ethanol (3 ml) is treated with 7 drops of 10% aq. $CaCl_2$ and then with 50 mg of zinc dust. The mixture is heated in a water bath, boiled for 1 min., filtered and cooled. Four drops of the filtrate are diluted to 2 ml and a drop of freshly prepared 1% aq. trisodium pentacyanoamminoferrate soln. is added. *o*-Nitrotoluene forms a pink or red colour, *m*-nitrotoluene a reddish-violet and *p*-nitrotoluene a violet-blue colour. The reaction does not occur in the absence of light. Nitrobenzene, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene interfere with the test by forming reddish-violet colours. Nitrobenzene is not normally present in commercial explosives; the other two interfering compounds can be distinguished by Janowski's reaction. A. O. JONES

1637. **Identification of adsorbed species by infra-red spectroscopy. Thiophen-cobalt molybdate systems.** D. E. Nicholson (Res. and Devel. Div., Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1365–1366.—Several possibilities for the structure of adsorbed thiophen are suggested by i.r. studies.

K. A. PROCTOR

1638. **New specific analytical procedures for the detection and characterisation of 1,4-naphthaquinones.** E. Sawicki and W. C. Elbert (R. A. Taft San. Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Anal.*

Chim. Acta, 1960, **23** (3), 205–208 (in English).—Certain derivatives of 1,4-naphthaquinone, *viz*, the 2-methyl-, 2-chloro-, 2,3-dichloro- and 2,3-dibromo-compounds, give a red colour when treated with 2-aminothiophenol in dil. HCl. The colour changes to blue with conc. HCl. Derivatives with an electron-donor group in the 2-position give negative results, as do other quinones. *Procedure*—Place a drop of reagent soln. (0·5 ml of 2-aminothiophenol and 4 ml of conc. HCl, diluted to 50 ml with water) on a filter-paper, followed by 1 μl of the methanolic test soln. in the centre of the drop. After a few minutes note the colour, then add a drop of conc. HCl and again note the colour. The identification limits are in all cases $< 0·5$ μg. Compounds giving a positive test may be differentiated by examination of their absorption spectra in acid soln. 2-Hydroxy-1,4-naphthaquinone (**I**) may also be detected by the following procedure. Place a drop of the reagent soln. (0·5 g of *o*-phenylenediamine dissolved in 4 ml of conc. HCl and 20 ml of water and then diluted to 50 ml with water) on a filter-paper, followed by 1 μl of the test soln. in acetic acid. Heat the spot in a jet of steam for 2 min., add a drop of 10% aq. KOH soln. and examine under u.v. light. A bright rose-red fluorescence indicates the presence of **I**. The identification limit is 0·3 μg. H. M.

1639. **Simple spot test for pyrene and its derivatives: application to air-pollution studies.** E. Sawicki and T. W. Stanley (R. A. Taft San. Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *Chemist Analyst*, 1960, **49** (3), 77–78.—*Procedure*—Evaporate the soln. to dryness, dissolve the residue in 0·1 ml of acetic acid - fuming HNO_3 (1 : 1) and heat at 100° for 5 min. Evaporate to dryness and add 1 drop of dimethylformamide. Place 1 drop of 25% aq. tetraethylammonium hydroxide soln. on filter-paper and apply 1 μl of test soln. to the centre. Pyrene and certain derivatives give a blue colour; identification limits range from 0·01 to 10 μg. Several common polynuclear hydrocarbons do not interfere. P. D. PARR-RICHARD

1640. **Determination of piperazine as piperazine diacetate.** G. R. Bond, jun. (Houdry Process Corp., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1332–1334.—*Procedure*—Melt the sample in a closed container at the minimum temp. and stir. Dissolve a portion (1 to 3 g) in acid-free acetone, dilute to 100 ml and mix. Dilute a 25-ml aliquot with acetone (25 ml), add an excess of glacial acetic acid (0·35 to 1·05 ml), stir well, set aside for 5 min. and filter through sintered glass. Dry the ppt. *in vacuo* over H_2SO_4 and weigh. The piperazine content of crude reaction mixtures over the range 1 to 100% can be determined with an accuracy of $\pm$ 0·2% absolute in the absence of alkylpiperazines, which are co-precipitated. Small amounts of water in the acetone do not interfere. A. R. ROGERS

1641. **High-resolution mass spectrometry. Interpretation of spectra of petroleum fractions.** E. G. Carlson, G. T. Paulissen, R. H. Hunt and M. J. O'Neal, jun. (Houston Res. Lab., Shell Oil Co., Texas, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1489–1494.—The instrument described is a double-focusing, coincident-field, mass spectrometer which has a resolving power approaching one order of magnitude higher than that of the conventional analytical instrument, and has been adapted for operation with high-boiling petroleum fractions New techniques are developed for petroleum components, and new molecular-type fractions are established. Applications, primarily with the mass region below m/e 400, are described for pure hydrocarbons, pure compounds of high molecular weight, carbon-number distribution of sulphur types, alkyl thiophens, non-hydrocarbon components in catalytic cracking streams and microcrystalline wax. C. B. BAINES

1642. **Rapid chemical determination of iron, nickel and vanadium in petroleum oils.** J. S. Forrester and J. L. Jones (Esso Res. Lab., Humble Oil & Refining Co., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1443–1446.—Low-temp. wet-ashing with HNO_3 - $HClO_4$, followed by chelation with 4,7-diphenyl-1,10-phenanthroline (**I**), furil α-dioxime (**II**) and 3,3′-dimethylnaphthidine (**III**) permits the rapid colorimetric determination of Fe, Ni and V, respectively, in petroleum oils. *Procedure*—To the oil (0·2 to 2 g) add satd. NaCl soln. (2 ml), HNO_3 (20 ml) and $HClO_4$ (15 ml) and heat until the exothermic reaction starts. Stop heating, then re-heat at intervals until the vol. is about 6 ml. Add H_2O (10 ml), boil for 1 min., cool and dilute to 25 ml. To determine Fe, add hydroxyammonium chloride soln. (10%) (2 ml) and Na acetate soln. (10%) (8 ml) to 5 ml of this soln., adjust to pH 3 to 4 with 20% NaOH soln., add 4 ml of **I** soln. (0·001M in ethanol) and extract with isoamyl alcohol (6 ml). Dilute the extract to 25 ml with ethanol and measure the extinction at 533 mμ in a 1-cm cell against a reagent blank. Calculate the Fe content from a calibration curve. To determine Ni, add 10% Na citrate soln. (5 ml), phenolphthalein (5 drops) and conc. aq. NH_3 (3 drops) to 10 ml of the original soln. Neutralise with 20% NaOH soln. and add 3 drops in excess. Add 3 ml of **II** soln. (1% in 50% ethanol) and extract with $CHCl_3$ (2 $\times$ 10 ml). Dilute the extract to 25 ml with $CHCl_3$, add 1 g of Na_2SO_3 and determine the extinction at 435 mμ in a 1-cm cell against a reagent blank. To determine V, add H_3PO_4 (2·5 ml) and **III** soln. (0·1% in glacial acetic acid) (2·5 ml) to 10 ml of the sample soln. and dilute to 25 ml. After 15 min. measure the extinction at 550 mμ against a reagent blank. J. P. STERN

1643. **Determination of halogens in polymers and other petroleum products by a two-furnace combustion method.** E. W. Seefield and J. W. Robinson (Esso Standard Div., Humble Oil and Refining Co., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (4), 301–305 (in English).—The problem of complete combustion of samples greater than 0·2 g has been overcome by the use of a furnace tube heated to 500° in one section and to 1000° in a second section. The sample (up to 20 g) is ignited in a stream of O (3 litres per min.) at 500° until combustion appears to be complete and is then pushed into the hotter zone for 10 min. The evolved gases are absorbed in a soln. containing NaOH (2%) and hydrazine sulphate (0·5%) and titrated potentiometrically with $AgNO_3$ (0·01N). T. R. ANDREW

1644. **Rapid combustion method for determination of phosphorus in petroleum products.** S. J. Gedansky, J. E. Bowen and O. I. Milner (Res. Dept., Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1447–1449.—A method is described in which the sample is mixed with anhydrous Na_2CO_3 before it is burned

in O in a closed flask. The phosphate that is formed is dissolved in dil. H_2SO_4 and can then be determined by the hydrazine - ammonium molybdate method. If much Ba is present the soln. may be centrifuged just before the colour measurement, but this is not usually necessary. The procedure is suitable for lubricating oils and additives. A sample of < 50 mg is required, containing between 0·013 and 0·4 mg of P. The precision (standard deviation $= 0{\cdot}0016$ for low concn. and 0·028 for high concn. of P) is equal to that of the ZnO method. The time required for one analysis is 20 min.

G. BURGER

1645. **Analytical separation of asphaltic constituents.** J. Buchta. *Ropa a Uhlie*, 1960, **2** (10), 268–269 (in Czech.).—The analytical separation of asphaltic constituents by chromatography on active alumina is described. Asphalt dissolved in CCl_4, after being fixed on the adsorbent, is eluted successively with CCl_4 (oil constituents), benzene (oil resins) and $CHCl_3$ (soft asphalts). The amount of asphaltenes is calculated by difference. Because of the efficiency of the chromatographic separation, it is suggested that this procedure should be used in preference to the determination of asphaltenes by hexane.

FUEL ABSTR.

1646. **Elemental interaction effects in the spectrochemical determination of additive elements in lubricating oils.** E. L. Gunn (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1449–1455.—A study of the interaction of Ca, Ba, P and Zn has been made in which a statistical design was employed. The direction and magnitude of interaction effects are well defined, and correction procedures are given. The effects of additive type, physical properties of the oil and instrumental variations are also considered, including a comparison of the porous-cup and rotating-disc techniques.

C. B. BAINES

1647. **Determination of total water in coal.** D. J. W. Kreulen (Lab. D. J. W. Kreulen, Rotterdam, Netherlands). *Chem. Weekbl.*, 1960, **56** (40), 548–549.—The determination of total water in coal containing inherent water is discussed. During evaporation of the water, the temperature of the coal may in some cases be so much decreased that the prescribed minimum temperature cannot be maintained, so that a low water content is obtained. In such cases it is proposed to dry the coal in air before drying in an oven, and to increase the drying time to 1 hr.

M. J. MAURICE

1648. **The use of partial demineralisation in coal analysis.** D. L. Ward and J. O'N. Millott (Nat. Coal Board, Coal Survey Lab., 20 Dee Hills Park, Chester, England). *Fuel, London*, 1960, **39** (4), 293–300.—Nearly all the mineral matter, except pyrites, is removed from coal by extraction with aq. HCl, aq. HF and conc. HCl, successively. The residue is washed with H_2O and dried *in vacuo*; C, H and calorific value are determined on the residue. A correction for absorbed HCl is obtained by determination of Cl in the coal, and for pyrites by determination of Fe in the ash. The corrected values are reported as based on the dry, ash-free coal. For coals with high ash content the results differ from those obtained by the normal method, based on mineral matter calculated by standard formulae, and are probably more accurate. The determination of volatile matter by this method gave variable results. Further investigation is needed.

G. BURGER

1649. **Rapid method for the quantitative determination of phosphorus in coal.** M. V. Voĭnalovich and G. V. Sipovskiĭ. *Dokl. Akad. Nauk Tadzh.SSR*, 1959, **2** (3), 11–15; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,114.—The photometric method described is based on the formation of molybdenum blue by reduction with hydrazine sulphate, and can be used to determine 3 to 70 μg of P. Ferric iron is first reduced to Fe^{2+} by Na_2SO_3 in acid medium. A correction must be made for the content of P in the reagents. Five parallel determinations can be carried out in a working day. The method is simple and rapid as compared with the titrimetric method, and gives reproducible results. The error in determining 0·065 to 0·5% of P is 0·01 to 0·02% absolute, and 2 to 3% relative.

C. D. KOPKIN

1650. **Analysis of metol - quinol developers by paper chromatography.** J. Šimek (Electrotech. Fac., ČVUT, Prague). *Chem. Průmysl*, 1960, **10** (8), 403–407.—The quant. determination of metol and quinol and their reaction products with alkaline Na_2SO_3 has been studied chromatographically. *Procedure*—Dilute the developer (50 ml) with glacial acetic acid (20 ml), place a suitable amount on Whatman No. 4 paper and treat by the ascending technique with n-butanol - acetic acid - H_2O (14 : 2 : 5), n-butanol - formic acid (85%) - H_2O (18 : 2 : 5) or ethyl acetate - acetic acid - H_2O (40 : 7 : 5) as solvent, detect the separated spots by spraying with a 3% soln. of $AgNO_3$ in aq. NH_3. Cut out the corresponding strips of the main paper, transfer to a titration vessel, dilute with H_2O (100 ml), add acetate buffer soln. (300 g of cryst. Na acetate, 900 ml of H_2O and 1 ml of glacial acetic acid) and an excess of 0·01N-iodine and after 30 sec. back-titrate with $Na_2S_2O_3$ soln., with starch as indicator. Quinol-mono- and -di-sulphonic acids, which are formed in developers by the action of alkaline Na_2SO_3, are determined by the same method, the back-titration being carried out after 10 min.

J. ZÝKA

1651. **A modern approach to the evaluation of bergamot oil.** F. C. Theile, D. E. Dean and R. Suffis (Shulton Inc., 630, 5th Avenue, New York 20). *Perfum. Essent. Oil Rec.*, 1960, **51** (10), 535–540.—The integration of spectrophotometric, i.r. and gas-chromatographic data together with pharmacopoeial tests is discussed as a means of detecting additions to natural bergamot oil. Natural bergamot oil displays u.v. absorption maxima at 270 mμ and 312·5 mμ ($E^{1\%}_{1\,cm} = 10$ to 13); the extinction values are directly proportional to the concn. of bergaptene, so that a low value indicates dilution. In the i.r. spectrum, linalyl acetate absorbs at 12·52 μ and 12·00 μ; the normal ratio of the absorption at 12·00 μ to that at 12·52 μ is 0·9 to 1·14, a lowering of this ratio indicating added terpenes. Chromatograms of the natural oil are characteristic and show the following area percentages—α-pinene, 7 to 10; (+)-limonene, 39 to 46; linalol, 17 to 24; and linalyl acetate, 22 to 30.

H. B. HEATH

1652. **Analysis of civet. Investigation of civet with the aid of urea.** F. Wolf (Anal. Lab. VEB Chem. Fabr. Miltitz, Leipzig). *Riechstoffe u. Aromen*, 1960, **10** (8), 261–266.—The sample is dissolved in $CHCl_3$ and treated with a methanolic soln. of urea (*Ibid.*, 1960, **10**, 33; 69) to remove hydrocarbons, waxes, etc., as adducts, and the liquid residue is examined for aroma-imparting

ingredients. Procedures are given for the formation of the adduct and its isolation and decomposition with hot water, and for the separation of the liquid residue from the adduct and the removal therefrom of $CHCl_3$ and methanol. The original sample is analysed for matter insoluble in $CHCl_3$ at 50° and for matter volatile at 105°; the product obtained on decomposition of the adduct is analysed for yield on the original sample, m.p., iodine value, and acid and ester values; the liquid residue is analysed for yield on the original sample, refractive index, acid, ester and hydroxyl values and content of carbonyl compounds (determined by the hydroxyammonium chloride method and calculated as civetone). H. L. WHITEHEAD

1653. **Detection and analysis of chlorosulphonated polyethylene.** G. G. Esposito (Aberdeen Proving Ground, Md., U.S.A.). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1960, **32**, 67–70.—A specific test for chlorosulphonated polyethylene, dependent on the reaction of SO_2Cl groups in the polymer, consists in adding to a solution of the resin (10 mg) in pyridine (3 ml), 2-aminofluorene (25 mg); a reddish colour develops within 1 hr. in the presence of the polymer. Sulphur and Cl may be determined after fusion with K_2CO_3 - Na_2O_2. The non-volatile content of the system, consisting of resin solution and curing agent, may be determined by stirring thoroughly, weighing large samples (5 to 10 g) into flat containers and heating for 3 hr. at 110°. L. A. O'NEILL

1654. **Polarographic determination of styrene in polystyrene.** J. Paściak (Chemical Works, Oświęcim, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 477–486.—After a brief review of available methods, a study of the polarographic method is described. Solutions of styrene and polystyrene (20% in benzene) were extracted with (*i*) 0·05M-tetrabutylammonium iodide (**I**) in 75% ethanol and (*ii*) 75% ethanol. The extract was separated by centrifuging and polarograms were run on aliquots of (*i*) as obtained and aliquots of (*ii*) after mixing with an equal volume of 0·1M-**I** in ethanol, both before and after removal of O with N; (*ii*) gave more reliable results, but only 0·1% of styrene could be determined, and the ratio of wave height to concentration was not linear for values $< 1{\cdot}6\%$. The errors were $\simeq 4\%$ for the range 0·1 to 4·5%. The substitution of dimethylformamide for ethanol resulted in improved sensitivity and accuracy and simplified the procedure. Polarograms are run on 2 ml of 0·1M-**I** in dimethylformamide to which 0·5 ml of the sample soln. in benzene (2·5 or 5%) has been added and O removed by passing a stream of N for 5 min.; $E_{\frac{1}{2}} = -2{\cdot}46$ *vs.* the S.C.E. The calibration curve is linear throughout the whole range studied, and 0·03% of styrene can be determined with an error of $\simeq 1{\cdot}5\%$. P. BRYCH

1655. **Hand-made shellac.** British Standards Institution (2 Park Street, London, W.1). B.S. 3280: 1960. 38 pp.—Five grades are specified, with methods for sampling, determination of matter insol. in hot alcohol, orpiment, rosin, volatile matter, matter sol. in H_2O, non-volatile matter sol. in cold alcohol, ash, grit, wax, acid value, iodine value, arsenic, lead and physical properties.

1656. **Seedlac.** British Standards Institution. (2 Park Street, Lonodn, W.1). B.S. 3279: 1960. 16 pp.—Six grades are specified, with methods for sampling, and the determination of volatile matter, wax, matter insol. in hot alcohol, non-volatile matter sol. in cold alcohol and matter sol. in water.

1657. **Determination of beeswax in wax compositions from the total paraffins, saponification, ester and acid values.** G. Spengler and A. Weber (Tech. Hochschule, München). *Fette, Seif., Anstrichmitt.*, 1960, **62** (10), 918–923.—A method is described in which the beeswax content can either be read from graphs of total paraffins, saponification, ester and acid values, or can be calculated from these results. The max. error is $\pm$ 3%. The presence of a foreign acid, or of a mixture of foreign acids or esters, can also be detected. I. DICKINSON

See also Abstracts—**1340**, Progress in elementary micro-analysis. Progress in functional-group micro-analysis. **1407**, Sulphate in detergents. **1425**, Decaborane in xylene. **1437**, Yttrium in coal ash. **1447**, Germanium and Ga in coal. **1473**, Ammonia in presence of amines. **1512**, Uranium in coal ash. **1530**, Detection of iodine in org. compounds. **1566**, Arsenic in coal and coke. **1760**, Dichlorophen on textiles.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

1658. **Tritium radioactivity determination of biological materials by a rapid dry-combustion technique.** E. A. Peets, J. R. Florini and D. A. Buyske (Pharm. Res. Dept., Expt. Therapeutics Res., Lederle Lab. Div., American Cyanamid Co., Pearl River, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1465–1468.—A furnace is described in which three samples of up to 2 g each can be simultaneously burned in O. The section of the furnace containing the catalyst (a roll of nickel foil and a pad of silver wool) is kept at 930° to 970° and the section containing the dried sample is heated steadily from room temp. to 700° in 30 min. Each of the three combustion tubes is connected to a cold trap. The tritium content of the collected water is determined in a liquid scintillation counter. The combustion of three samples takes 45 min. G. BURGER

1659. **Methods for the destruction of organic matter.** The Metallic Impurities in Organic Matter Sub-Committee of The Analytical Methods Committee of The Society for Analytical Chemistry. *Analyst*, 1960, **85**, 643–656.—The methods described are—(*a*) destruction with HNO_3 and H_2SO_4 with or without $HClO_4$ or H_2O_2; (*b*) destruction with HNO_3 and $HClO_4$; (*c*) destruction with HNO_3 and NH_4NO_3; and (*d*) special methods of wet decomposition for the determination of Hg. In the six methods described for dry-ashing, the ashing aids used are, respectively, none, MgO, $Mg(NO_3)_2$ soln., anhyd. Na_2CO_3, Na_2CO_3 soln. and H_2SO_4. The choice of ashing aid is governed by the nature of the sample or by the nature of the metal under investigation. In both wet and dry procedures, indications are given of the circumstances in which each procedure may be used. A. O. JONES

1660. **Titrimetric tetraphenylborate determination of potassium and application to blood serum and plant material.** F. Bermejo Martínez and Monserrat Gonalons Bori (Fac. of Sci., Univ.,

Santiago de Compostela, Spain). *Chemist Analyst,* **1960, 49** (3), 69–71.—To determine K in blood serum the sample is deproteinised with sodium tungstate and H_2SO_4. Plant material is digested with HNO_3 and H_2SO_4. *Procedure*—To 1 ml of soln. (0·006 to 3 mg of K) add 20% NaOH soln. to pH 9, 0·5 ml of 35% formaldehyde soln. and approx. 1 ml in excess of purified 1·2% Na tetraphenylborate (**I**) soln. in dil. NaOH soln. (pH 9). Dilute to 25 ml, set aside for approx. 3 min. and filter. Titrate 5 ml of the clear filtrate with a quaternary ammonium salt soln., with bromophenol blue as indicator. To standardise the soln. of **I**, mix 2 ml of KCl soln. [1·25 g of KCl, 50 ml of 4% ammonium oxalate soln. and 5 ml of aq. NH_3 (1:1), diluted to 250 ml] with 1 drop of 20% NaOH soln., 0·5 ml of formaldehyde soln. and 5 ml of **I** soln. Dilute to 25 ml and proceed as described above. P. D. PARR-RICHARD

1661. **Complexometric determination of potassium in the presence of ammonium.** A. Holasek, H. Lieb and M. Pećar (Univ. Graz, Austria). *Mikrochim. Acta,* **1960**, (5–6), 750–754 (in German).—For the determination of K in urine by pptn. with $Na_3Co(NO_2)_6$ and complexometry of the Co in the ppt., the concn. of NH_4^+ must be < 0·02N; the NH_4^+ can then be masked with formaldehyde (**I**), 1 ml of 30% **I** soln. masking 720 μg of NH_4^+. The accuracy on 300 to 600 μg of K in 2 ml of 0·005N NH_4^+ soln. is within ± 1·6%. *Procedure*—To the sample (2 ml) add 50% Na acetate soln. (5 ml), **I**, and 30% $Na_3Co(NO_2)_6$ soln. (1 ml). Set aside overnight in the cold, filter and wash the ppt. with cold water. Dissolve the ppt. in boiling 0·25N-HCl (5 ml) containing a little urea, add 50% Na acetate soln. (0·5 ml) and heat to boiling. To the hot soln. add a few crystals of ascorbic acid, 2 drops of 0·1M-Cu - EDTA and 2 to 4 drops of 0·05% ethanolic 1-(2-pyridylazo)-2-naphthol soln. Titrate with 0·001M-EDTA (disodium salt) to a yellow end-point. J. P. STERN

1662. **Determination of magnesium in plant material with Titan yellow.** E. G. Bradfield (Res. Sta., Long Ashton, Bristol, England). *Analyst,* **1960, 85**, 666–670.—Since Titan yellow varies in composition, a spectrophotometric standardisation of its soln. in 0·1% aq. poly(vinyl alcohol) is made at 550 mμ to ensure adequate concn. of the component that precipitates Mg. The ground and dried plant material (1 g) is digested with HNO_3 and, after addition of $HClO_4$, heating is continued until nearly all the $HClO_4$ has been removed. The cooled residue is diluted, boiled and filtered, and the vol. is adjusted to 100 ml. An aliquot is adjusted to pH 3 to 4 with aq. NH_3 and applied to an exchange column of De-Acidite E (Cl^- form), and the column is eluted with water until 100 ml has been collected. An aliquot of the eluate and a series of standards (0 to 100 μg of Mg) are treated with 2 ml of a compensating soln. containing $CaCl_2$, $AlCl_3$, hydroxyammonium chloride and triethanolamine, and are heated in water at 25°, after which a 4-ml portion of Titan yellow - poly(vinyl alcohol) reagent is added and then immediately 4 ml of NaOH soln. (8% w/v). After 30 min. the extinctions are measured at 550 mμ. Results with some plant materials are quoted and compared with those found by the 8-hydroxyquinoline method. A. O. JONES

1663. **Acid Alizarin black SN, a metallochromic indicator for calcium.** R. A. Close and T. S. West (Univ., Birmingham, England). *Anal. Chim. Acta,* **1960, 23** (3), 261–267 (in English).—Acid Alizarin black SN (C.I. Mordant Black 25) (**I**) and Acid Alizarin black SE (C.I. Mordant Black 10) (**II**) have been examined as complexometric indicators. Only **I** is of any value and is stated to be the best indicator for Ca in dilute (≯0·02M) soln. The colour change is from purple to red just before the end-point, which is marked by a very sharp change to blue. The preferred pH is 11·5 to 12·5; Sr behaves similarly, and Cd gives a sharp change from red to blue at pH 8·5. The change with Mn is from purple to blue at pH 10, and with Ni and Zn it is from purple to blue at pH 11·5 in hot soln. Thorium gives a sharp change from crimson to orange at pH 4. It is concluded from spectrophotometric evidence that the complex with Ca is a 2:1 chelate of indicator with Ca. H. M.

1664. **Photometric titration of calcium in blood serum with Acid Alizarin black SN as metallochromic indicator.** R. A. Close and T. S. West (Univ. Birmingham, England). *Anal. Chim. Acta,* **1960, 23** (4), 370–374 (in English).—The sample of serum (100 μl) is diluted to 2·5 ml, 0·2M-triethanolamine (1 drop), N-NaOH (0·5 ml) and 0·1% Acid Alizarin black SN (C.I. Mordant Black 25) soln. (3 drops) are added, and the soln. is titrated with $2{\cdot}5 \times 10^{-3}$M-EDTA (disodium salt) in an E.E.L. photo-electric titrator with a filter at 660 mμ. T. R. ANDREW

1665. **Colorimetric determination of iron in plasma.** E. Scala, A. Castaldo and G. Ruiz (Ist. Chim. Biol., Univ. Napoli, Italy). *Boll. Soc. Ital. Biol. Sper.,* **1960, 36** (19), 1048–1052.—The method involves liberation of iron from its globulin complex by treatment with hot dil. HCl, removal of protein by treatment with trichloroacetic acid, and colorimetric determination of Fe in the resulting soln. after addition of KSCN. It is preferable (but not essential) to use plasma treated with heparin as an anticoagulant. *Procedure*—Prepare a 0·5% soln. of heparin and transfer 0·2 ml to a centrifuge tube and dry in an incubator for 24 hr. To the residue add venous blood (4 ml), centrifuge immediately, and separate the plasma. To the plasma (2 ml) add 0·3N-HCl (1 ml) and place in a water bath at 56° for 20 min. Add 20% trichloroacetic acid soln. (2 ml), mix and centrifuge for 10 min. at 2000 r.p.m. Remove the clear supernatant liquid (2 ml) and add 29% KSCN soln. (0·8 ml) and a fresh satd. soln. of $K_2S_2O_8$ (0·2 ml). Measure the extinction at 390 mμ and compare with standards treated similarly. Interference by iron in haemoglobin is small (< 0·02% of the total Fe present) and the recovery of added Fe exceeds 95%. E. C. APLING

1666. **Macro- and micro-determination of traces of cobalt. VI. Determination of cobalt in blood.** W. Haerdi, J. Vogel, D. Monnier and P. E. Wenger (Lab. de Chimie Minérale, Univ. Genève). *Helv. Chim. Acta,* **1960, 43** (3), 869–877 (in French).—The Co in the sample is recovered as the nitroso-R salt complex and determined spectrophotometrically. Losses (which amount to 10 to 30% of the metal) are allowed for by addition of a known amount of ^{60}Co as an internal tracer. To 50 to 100 mg of blood is added 4 ml of a soln. of a ^{60}Co salt containing 0·003 μg of ^{60}Co (0·017 μC) and the mixture is evaporated in a quartz vessel under an infra-red lamp at 160° to 180°; the residue is heated in an oven at 450° to 500° to remove the carbon. The residue is dissolved by warming in 40 ml of 9M-HCl. The soln. is passed through a

Dowex 1-X8 column (10 g, washed, demineralised with 0·01M-HCl and then saturated with 9M-HCl), the column is washed with 9M-HCl and the Co eluted with 30 ml of 4M-HCl in 4-ml portions, of which the second and third are taken for analysis; these are evaporated in a quartz vessel, in the presence of 5% NaCl soln. under an infra-red lamp, and the organic residue is destroyed by heating with 0·5 ml of HNO_3 (1·5 ml) and subsequently with $HClO_4$. The residue is dissolved in 1 ml of HCl, again evaporated and dissolved in 0·4 ml of water and 0·4 ml of 10% Na acetate soln. The γ-radiation of the soln. is measured. This permits the calculation of the actual Co loss. Finally, 0·1 ml of a 0·05% soln. of nitroso-R salt is added, followed by 0·1 ml of HNO_3 and heating to destroy the excess of reagent. The mixture is centrifuged at 3000 r.p.m. for 20 min. The extinction of the soln. is measured and the Co content calculated.
J. L. PROSSER

1667. **Determination of vanadium and cobalt in plants by neutron activation analysis of paper chromatograms.** H. W. Yurow. *Dissert. Abstr.*, 1960, **21** (1), 46–47.—A soln. of the plant ash at pH 1·5 was treated with cupferron and $CHCl_3$ to extract Cu, Fe, Ti, V and Mo. A further extraction at pH 4·0 with diethyldithiocarbamic acid (**I**) and CCl_4 removed Co, Ni and Zn. Paper chromatography of the cupferron extract with ammoniacal butanol - dimethylglyoxime separated V from other constituents. Chromatography of the **I** extract with 1,2-dimethoxyethane - H_2O separated Co from Zn and partially from Ni (which does not interfere). The chromatograms were irradiated with thermal neutrons which formed ^{52}V and ^{60m}Co. The radioactivities of these isotopes were measured with a Geiger - Müller counter and related to the amount of element present. N. E.

1668. **Rapid estimation of uranium in urine using the type 1080A fluorimeter.** U.K.A.E.A. (Production Group, Chemical Services Dept., Springfields, Lancs., England). U.K.A.E.A. Report PG 57(S), 1960. 9 pp.—Full experimental details are given of a procedure in which the urine (1 ml) is evaporated to dryness and the residue, after ignition, is fused with a mixture of $NaHCO_3$ and NaF (9 : 1) at 1000° for 1 min. The cooled mass is then examined in the fluorimeter and the content of U is derived by applying a factor that has been obtained, either by calibration involving the use of known quantities of U, or by making a standard addition of U to two of the four samples analysed. The limit of detection is 5 μg of U per litre; the coefficients of variation for the two methods of calibration are 15 and 12%, respectively.
G. J. HUNTER

1669. **Rapid ultra-violet spectrophotometric determination of salicylate in blood.** G. W. Stevenson (Dept. of Pharmacol. and Toxicol., Sch. of Med., Univ. of Calif., Los Angeles, U.S.A.). *Anal Chem.*, 1960, **32** (11), 1522–1525.—Salicylate (up to 50 mg per 100 ml) can be extracted from whole blood or any blood fraction, and simultaneously acidified, by shaking the sample with a soln. of malonic acid in butyl ether. The extinction of the extract is determined at 378, 314, 307, 300 and 280 mμ, and the salicylate concn. is calculated from given equations. A further extraction of the ether extract with phosphate buffer is described, but offers no significant advantage. G. BURGER

1670. **Comparison of radiochemical and colorimetric methods for the determination of sulphaphenazol in blood and tissues.** K. Schmid, J. Tripod and F. Gross (Forschungslab., CIBA, A.-G., Basel, Switzerland). *Klin. Wochschr.*, 1960, **38** (17), 862–866.—The colorimetric method of Bratton and Marshall (*J. Biol. Chem.*, 1939, **128**, 537) for sulphonamides, as applied to sulphaphenazol [5-(*p*-aminobenzenesulphonamido)-1-phenylpyrazole], is compared with a radio-isotope method with ^{35}S-labelled material. The methods agreed closely in the values obtained for concn. in blood, urine and faeces, but the radiochemical method gave very much higher results than the colorimetric method for tissues. The reason for this is undetermined. H. F. W. KIRKPATRICK

1671. **Detection and determination of aniline in forensic studies.** E. A. Gryaznova and V. G. Belikov. *Sudebnomed. Ekspertiza*, 1959, **2** (4), 39–43; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 47,256.—A new specific colour reaction is described for the detection and determination of aniline (**I**) in biological material with a soln. of sodium nitroprusside (**II**) irradiated with u.v. light. Separate the **I** from the biological material by steam-distillation; to 1 ml of the distillate add a few drops of 2% Na_2CO_3 soln. and 1 ml of 1% **II** soln. that has been irradiated with a quartz lamp for 20 min. At a concn. of **I** of 50 μg per ml a blue colour appears after a few seconds; at lower concn. the colour develops more slowly. There is no interference from HCN, $CHCl_3$, chloral, hexachlorocyclohexane, phenol, nitrobenzene, benzene, toluene or formaldehyde. To determine **I**, to 100 g of cadaveric material add a known amount of **I** (100, 150, 200, 250 or 300 μg) and, after setting aside for 2 or 3 hr., steam-distil; measure the vol. of distillate and to 10 ml add 3 ml of 2% Na_2CO_3 soln. and 7 ml of **II** soln.; after 20 min. measure the extinction in a Duboscq colorimeter, with a standard scale for comparison. The recovery of the **I** present in biological material is 73·5 to 93·5%, and the method is as sensitive as the bromatometric method. C. D. KOPKIN

1672. **Detection and estimation of trace amounts of 3,4-benzopyrene in biological material.** J. Pavlů and J. Šula (Fac. of Med., Charles' Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (9), 2461–2463 (in English).—The sample is treated with ethanolic KOH, set aside for 12 hr. and then heated under reflux for 5 hr. and then extracted with light petroleum. The extracts are washed with H_2O, dried over $CaCl_2$ and evaporated to dryness. The residue is dissolved in benzene and the soln. is chromatographed on a column of alumina, with benzene as the eluent. The eluate is concentrated and resolved by chromatography on acetylated paper with methanol - ether - water (4 : 4 : 1). The chromatograms are examined under u.v. light, the presence of 3,4-benzopyrene being shown by blue - violet spots. When the concn. is > 2 μg per 50 g of sample, the benzopyrene is determined absorptiometrically at 389 mμ on the eluate from the spots. The method is applicable to liver tissue and, with some modification, to anthracotic lymphatic nodes. G. P. COOK

1673. **Diagnostic composition** [**for oral administration to determine gastric acidity**]. Cilag-Chemie, Ltd., formerly Cilag, Ltd. Brit. Pat. 850,426; date appl. 28.10.58. Switzerland, date appl. 5.11.57.—The composition comprises 2,6-diamino-3-phenylazopyridine, or a 3-(*p*-alkylphenylazo)- or

a 3-(p-alkoxyphenylazo)-2,6-diaminopyridine in which the alkyl or alkoxy-groups contain 1 to 4 carbon atoms, in admixture with an amphoteric protein (zein) that is practically insol. in water and in N-HCl and of which the iso-electric point lies at a pH below 7. The amount of dye excreted is dependent on the pH conditions in the stomach, and is determined colorimetrically on a sample of urine, 1·5 hr. after ingestion, after acidification with HCl. J. M. JACOBS

1674. **Colorimetric determination of 3,6-anhydrogalactose and galactose in marine algal polysaccharides.** W. Yaphe (Atlantic Reg. Lab., National Res. Council, Halifax, Nova Scotia, Canada). *Anal. Chem.*, 1960, **32** (10), 1327–1330.—To determine 3,6-anhydrogalactose (**I**), mix the sample soln. (2 ml, containing 5 to 40 μg of **I** or 30 to 200 μg of polysaccharides) with reagent [add 0·13% ethanolic resorcinol soln. (10 ml) to 12M-HCl (100 ml) immediately before use] (10 ml), mix, heat for 10 min. at 80° ± 0·2°, cool in ice for 90 sec. and measure the extinction at 550 mμ. To determine **I** and galactose (**II**) together, and hence **II** by difference, cool a 0·2% soln. of anthrone in 80% (v/v) H_2SO_4 (10 ml) for 5 min. in ice, add the sample soln. (2 ml), set aside in ice for 2 min., mix well, heat at 80° for 20 min., cool in ice for 5 min. and measure the extinction at 625 mμ against a reagent blank. Alternatively, use the extinction of soln. heated with anthrone reagent for 5 min. and 20 min. to calculate the concn. of **I** and **II** simultaneously by the equations of Brown *et al.* (*J. Lab. Clin. Med.*, 1957, **49**, 630). The accuracy by either method is within $\simeq \pm 6\%$. A. R. ROGERS

1675. **Thiamine and its mono-, di- and triphosphoric ester content of normal rat tissues.** G. Rindi and L. de Guiseppe (Ist. Fisiol., Univ. Pavia, Italy). *Experientia*, 1960, **16** (10), 447 (in English).—A protein-free extract of tissue homogenised in 5% trichloroacetic acid is adjusted to pH 6·7 to 6·8 with 40% NaOH soln. and passed through a charcoal column. After being washed with H_2O, the column is eluted with 60 to 70 ml of 10% n-propanol, and the eluate is concentrated to 5 ml at 25° to 30° *in vacuo*. The concentrate and washings (15 ml), after addition of 0·8 ml of 0·1N-HCl, are chromatographed on a column of Dowex 1-X8 (acetate form), which is eluted with 10 ml of H_2O. The thiamine and its monophosphate are determined in this eluate by difference before and after Taka-diastase digestion. The thiamine pyrophosphate is eluted from the column with 20 ml of 0·02M-Na acetate in 0·04M-acetic acid, and the triphosphate with 20 ml of M-acetate buffer at pH 4·5. After Taka-diastase hydrolysis, the pyrophosphate content is determined directly, and the triphosphate content after percolation through Amberlite IRC-50 buffered at pH 4·5. Recovery of the extracted thiamine compounds is about 95%. D. E. EVANS

1676. **Two new solvent systems for the countercurrent distribution of carotenoids.** A. L. Curl (Western Utilisation Res. and Devel. Div., U.S. Dept. of Agric., Albany, Calif.). *J. Agric. Food Chem.*, 1960, **8** (5), 356–358.—A clean separation of diol, monoepoxide diol, diepoxide diol and polyol fractions was obtained with light petroleum - methanol (26·5: 73·5) by countercurrent distribution in a Craig apparatus (*cf. Ibid.*, 1953, **1**, 456). The carotenoid polyols can be further fractionated by light petroleum - acetone - methanol - water (1·25: 1·0: 0·10: 0·65). Graphs are given showing the distribution of the diols and polyols contained in orange juice and pulp, cling peaches, and pyracantha leaves. Spectral absorption maxima in benzene and N_{100} values (N_{100} = tube no. of max. per 100 transfers) are also given for individual fractions. R. A. HENDEY

1677. **Determination of urinary porphyrins.** H. Holland (Katharinenhospital-Apotheke, Stuttgart, Germany). *Dtsch. ApothZtg*, 1960, **100** (38), 1096–1098.—A review is presented of methods for the rapid routine paper-chromatographic separation of the methyl esters of uroporphyrins I and III, coproporhyrins I and III, and protoporphyrin IX, and for the determination of the porphyrins and porphobilinogen in urine. (17 references.) A. R. ROGERS

1678. **Infra-red absorption analysis of tissue constituents, particularly tissue lipids.** H. P. Schwarz. *Adv. Clinical Chem.*, 1960, **3**, 1–34.—A review article.

1679. **Chromatography of lipids on silicic acid.** J. J. Wren (Lyons Laboratories, Hammersmith Road, London, W.14). *J. Chromatography*, 1960, **4** (3), 173–195.—A review is presented with 290 references. The items dealt with comprise the adsorbent, the eluents, experimental considerations and the order of elution of the different lipid classes. R. M. S. HALL

1680. **Improved method for the detection of lipid on paper chromatograms.** L. L. Sulya and R. R. Smith (Sch. Med., Univ. Mississippi, Jackson, Tenn., U.S.A.). *Biochem. Biophys. Res. Commun.*, 1960, **2**, 59–62.—When paper chromatograms of lipids are dipped in a soln. of protoporphyrin in HCl and, after being washed in water, are examined in u.v. light, the lipids appear as brilliant red spots on a blue background. The wide range of lipids detectable by this technique includes fatty acids, triglycerides, lecithin, lysolecithin, sphingomyelin, cholesterol, and cholesteryl esters. NUTR. ABSTR. REV.

1681. **Micro-determination of long-chain fatty acids in plasma and tissues.** V. P. Dole and H. Meinertz (Rockefeller Inst., New York 21, U.S.A.). *J. Biol. Chem.*, 1960, **235** (9), 2595–2599.—Modifications of the original method of Dole (*J. Clin. Invest.*, 1956, **35**, 150) are given. A single extraction of plasma with the two-phase system heptane - isopropyl alcohol - water has sufficient analytical specificity for the subsequent determination of long-chain fatty acids. If exceptional amounts of lactic, acetic, acetoacetic or β-hydroxybutyric acids are present they are eliminated by a second extraction. The two-phase system is also useful for countercurrent distribution. A table of partition coeff. for various acids is given from which the number of transfers needed for analytical work can be calculated. A simple eight-transfer procedure, which needs $< 0·5$ hr., separates the acids of an extract into long-chain fatty acids, cephalins and polar org. acids. J. N. ASHLEY

1682. **Detection of some urinary amines.** J. Ratcliffe and P. Smith (R.A.F. Inst. of Aviation Med., Farnborough, Hants, England). *Chem. & Ind.*, 1960, (37), 1159.—4-Methoxyadrenaline, 4-methoxynoradrenaline and monohydroxy- and 4-hydroxy-3-methoxyphenyl-ethylamines, and, provisionally, 4-hydroxyphenylethanolamine (octop-

amine) and phenylephrine, its *N*-methyl homologue, have been detected in urine. The amines in a 15-min. excretion aliquot were gently hydrolysed from the sulphate forms and then adsorbed on an ion-exchange resin (Na^+ form). After elution with 3N-aq. NH_3 the amines were separated from the many non-basic substances and identified by paper chromatography. R. M. S. HALL

1683. **Water-elution chromatography of amino-acids on ion-exchange materials.** D. L. Buchanan and R. T. Markiw (Veterans Admin. Hospital, West Haven, Conn., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1400–1407.—Several ion-exchange resins of weak or intermediate acidity or basicity have been examined for their ability to separate mixtures of amino-acids with H_2O as the eluent. Several complete and many incomplete separations are reported. The results indicate the possibility of achieving many more complete separations by the use of more suitable resins or blends of resins. G. BURGER

1684. **Determination of carbon and its radio-activity. III. Transfer of small samples of carbon dioxide to counting tubes.** D. D. Van Slyke and J. Plazin (Med. Res. Centre, Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *J. Biol. Chem.*, 1960, **235** (9), 2749–2752.—A micro-manometric modification of the ninhydrin - CO_2 method for the determination of the carboxyl CO_2 of α-amino-acids is described, together with a procedure for the transfer of the CO_2 to a Bernstein - Ballentine gas counter for counting the $^{14}CO_2$. The method is applicable to the determination of 10 to 30 μg of carboxyl C. When CO_2 is transferred from a manometric chamber to a gas counter as described by Van Slyke *et al.* (*Brit. Abstr. C*, 1952, 82), a small vol. of CO_2, sufficient to be significant with samples of < 2 mg of C, may be trapped in the connecting tube. This can be washed quant. into the counter by a few ml of methane, admitted into the manometric chamber after the usual transfer operation. J. N. ASHLEY

1685. **Ninhydrin as a reagent for *N*-methylamino-acids.** D. W. Russell (Plant Chem. Div., D.S.I.R., Palmerston North, New Zealand). *J. Chromatography*, 1960, **4** (3), 251–252.—*N*-Methyl derivatives of glycine, valine, leucine and isoleucine have been tested. Peart's method (*Biochem. J.*, 1956, **62**, 520) has been used for quant. determination. For qual. use a 1 : 1-mixture of 0·33% ninhydrin in t-butyl alcohol and glacial acetic acid - water - pyridine (1 : 5 : 5) has been used and the paper is heated to 110° for 15 min. The limit of detection is 0·01 μmole. Both amino- and *N*-methylamino-acids give purple colours; *N*-methylamino-acids are distinguished by the very faint colours given with ninhydrin in water-satd. n-butanol containing 2% of glacial acetic acid. R. M. S. HALL

1686. **Paper-chromatographic identification of cyclic imino-acids.** G. Parmentier and H. Vanderhaeghe (Rega Inst., Univ., Louvain, Belgium). *J. Chromatography*, 1960, **4** (3), 228–232.—The positions on a chromatogram are illustrated and the R_F values are tabulated for these compounds after two-dimensional development with (*i*) n-butanol - acetic acid - water (4 : 1 : 5) and (*ii*) water-satd. phenol. This order yields better results than the reverse one. Confirmatory colour reactions with various reagents, *viz.* ninhydrin, isatin, ninhydrin - isatin - triethylamine (Kolor and Roberts, *Anal. Abstr.*, 1958, **5**, 652) and *p*-nitrobenzoyl chloride - pyridine (Plattner and Nager, *Helv. Chim. Acta*, 1948, **31**, 2203) are also tabulated and discussed. R. M. S. HALL

1687. **Qualitative separation of choline esters by means of high-voltage paper electrophoresis.** E. Heilbronn and B. Carlsson (Res. Inst. of National Defence, Sundbyberg, Sweden). *J. Chromatography*, 1960, **4** (3), 257–259.—The mobilities are reported of 18 choline esters in buffer soln. of pH 10·0, 9·1, 5·0 and 4·6 for electrophoresis at 12° to 13° for 30 to 60 min., at 30 V per cm (1500 V). After drying and spraying with dipicrylamine, choline and acetylcholine gave blue - red spots, and other choline esters gave orange - red ones. Molybdophosphoric acid is more reliable, but less sensitive, than dipicrylamine. R. M. S. HALL

1688. **Improvements in test compositions for protein [in biological fluids].** A. Galat. Brit. Pat. 852,669; date appl. 5.11.58.—A reagent for the detection of albumin in urine comprises a solution of an ester (ethyl ester) of bromophenol blue (in the form of a salt, *e.g.*, the potassium salt) and a weak org. acid (acetic acid) in a water-sol. tertiary alcohol (t-butyl alcohol, or diacetone alcohol). J. M. JACOBS

1689. **Albumin diagnostic compositions.** Miles Laboratories, Inc. Brit. Pat. 853,643; date appl. 20.3.59. U.S.A., date appl. 25.3.58.—An indicator for determining albumin in urine, etc., comprises strips of filter-paper impregnated with a soln. consisting of 10 ml of a buffer, composed of 2M-sodium citrate (2·2 pt.) and 2M-citric acid (7·8 pt.), and 10 ml of a 0·08% soln. of bromophenol blue in 95% ethanol. (Addn. to Brit. Pat. 826,066; *cf. Anal. Abstr.*, 1960, **7**, 1871.) J. M. JACOBS

1690. **Optimal staining conditions for the quantitative analysis of human serum protein fractions by cellulose acetate electrophoresis.** C. J. Brackenridge (Royal Perth Hosp., W. Australia). *Anal. Chem.*, 1960, **32** (10), 1353–1356.—The use of Lissamine Green (C.I. Acid Green 5) with the electrophoretic method of Kohn (*Clin. Chim. Acta*, 1958, **3**, 450) is investigated and its suitability for quantitative work is established. The dye-binding capacities of five protein fractions are determined, and are virtually linear with respect to concn. The recommended pH for the dye bath is 2·7, and for the eluting soln. 6·0. Temp. has a marked effect on the dye uptake and thermostatic control is essential to the staining process. H. F. W. KIRKPATRICK

1691. **Optimal fractionation conditions for the quantitative analysis of human serum protein fractions by cellulose acetate electrophoresis.** C. J. Brackenridge (Royal Perth Hosp., W. Australia). *Anal. Chem.*, 1960, **32** (10), 1357–1359.—The variables investigated are the choice of buffer, its ionic strength and pH and the vol. used; the effects of voltage and running time of electrophoresis, of the length of strip, and of the position of application of the serum. The final technique is described in detail. H. F. W. KIRKPATRICK

1692. **Comparative studies on protein hydrolysis with a view to reducing the destruction of components of the protein. I. Quantitative estimation of amino-acids in protein hydrolysates with the aid of an automatic recording apparatus.** G. Krampitz (Inst. Anat. Physiol. Haustiere, Univ. Bonn). *Z. Tierernähr.*, 1960, **15**, 40–46.—The apparatus is described.

II. Behaviour of free amino-acids in conditions of protein hydrolysis. G. Krampitz. *Ibid.*, 1960, **15**, 76–86.—Of the amino-acids studied, only tryptophan, cysteine and methionine were detectably degraded by treatment with 6N-HCl for 24 hr. under the conditions for protein hydrolysis.

III. Hydrolysis of pure proteins. G. Krampitz. *Ibid.*, 1960, **15**, 87–95.—A combination of conditions of hydrolysis was devised for bovine serum albumin to give complete recovery of all amino-acids. NUTR. ABSTR. REV.

1693. **Cystine content of proteins, foods and feeds. Comparison of chromatography on a sulphonated polystyrene resin and microbiological methods of determination.** R. J. Evans, S. L. Bandemer and D. H. Bauer (Dept. of Agric. Chem., Michigan State Univ., East Lansing, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (5), 383–386.—The cystine contents of several proteins, foods and feeding-stuffs have been determined by chromatography (*cf.* Schram *et al.*, *Anal. Abstr.*, 1954, **1**, 1936) and three microbiological procedures. In the microbiological procedures, *Leuconostoc mesenteroides* P-60 was used as the organism in the peptone medium method (Lyman *et al.*, *Arch. Biochem.*, 1946, **10** 427), with a 30-min. and a 6-hr. hydrolysis period, and, in the lanthionised casein method (*cf.* Horn and Blum, *Cereal Chem.*, 1956, **33**, 18), with a 30-min. hydrolysis time. Chromatography of cysteic acid gave the most reproducible results, and was considered the most satisfactory. The two microbiological procedures with a 30-min. hydrolysis period generally gave higher results than did chromatography, while the 6-hr. hydrolysis method gave lower results. Reasons are suggested for the erratic results of the microbiological assays, and tables of results are given for the cystine content of many foods and feeding-stuffs by using all the methods described. R. A. HENDEY

1694. **Variable dye uptake in the quantitative analysis of abnormal globulins by cellulose acetate electrophoresis.** C. J. Brackenridge (Royal Perth Hosp., W. Australia). *Anal. Chem.*, 1960, **32** (10), 1359–1360.—The concn. of an abnormal protein is best determined by an independent method, as the dye uptake appears to be impossible to predict. H. F. W. KIRKPATRICK

1695. **New paper-chromatographic technique for the separation of cholesterol and cholesteryl esters.** Č. Michalec and J. Strašek (Lab. of Protein Metab. & Proteosynthesis, Charles' Univ., Prague, Czechoslovakia). *J. Chromatography*, 1960, **4** (3), 254–257.—The reversed-phase partition system has been further modified. The paper (Whatman No. 3) is drawn through a soln. of 0·5% (v/v) of liquid paraffin (sp. gr. 0·880) in ether. After a few minutes the strips are ready and can be kept for more than 1 month. Development with acetic acid satd. with liquid paraffin for 5 to 6 hr. is used for C_2 to C_8 derivatives, and with acetic acid - $CHCl_3$ - liquid paraffin (16:1:1) for 3 to 4 hr. for cholesterol derivatives. By this procedure, the mobilities of the compounds differ more, and complete resolution is attained more rapidly; no previous equilibration is necessary. Saturated and unsaturated compounds cannot be resolved with these systems alone. R. M. S. HALL

1696. **Characterisation of some steroid hormones through micro-sublimation.** E. Kassau (Univ.-Klinik., Bonn, Germany). *Dtsch. ApothZtg*, 1960, **100** (38), 1102–1106.—The appearance of the sublimates is described and limits of detection (mostly < 1 μg) are given. There are 45 photomicrographs. A. R. ROGERS

1697. **Determination and significance of the natural oestrogens.** J. B. Brown. *Adv. Clinical Chem.*, 1960, **2**, 157–233.—A review article.

1698. **Effect of interfering chromogens in spectrophotometric determination of ruminant urinary androgens.** W. S. Ruliffson, A. M. Gawienowski and J. S. Hughes (Agric. Exp. Sta., Kansas State Univ., Manhattan, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (5), 395–397.—The effect of certain non-steroid ketones and non-17-oxosteroids has been investigated with respect to the determination of androsterone (**I**) and dehydroepiandrosterone (**II**). Absorption spectra are given for the colours produced in the Allan, Pincus and Zimmermann reactions, with pure **I** and **II** and ruminant urine with added **I** and **II**. In each case the absorption peaks, although characteristic, were different and, in general, moved to shorter wavelengths. Unidentified substances normally present in the urine are responsible for these effects and may enhance or change the normal spectra of small amounts of oxosteroids present in the urine. R. A. HENDEY

1699. **Method for determination of 21-deoxyketol steroids.** P. Cristol and M. F. Jayle (Fac. de Médicine, 45 rue des Saints-Pères, Paris). *Bull. Soc. Chim. Biol.*, 1960, **42** (5–6), 655–663.—A method is discussed and developed whereby 21-deoxyketol steroids (**I**) are reduced to the acetaldehydogenic steroids by means of alkali borohydride. The acetaldehyde formed is determined by the method of Cox [*Biochem. J.*, 1952, **52**, 340 (macro-method); *Anal. Abstr.*, 1960, **7**, 1879 (micro-method)]. *Procedure with urine* (*macro-method*)—Collect a 24-hr. sample of urine, with 1 ml of 2% $Hg(CN)_2$ soln. and 2 ml of $CHCl_3$ as antiseptics. To 25 ml add 2·5 ml of acetate buffer (pH 5·2) and 0·25 ml of *Helix pomatia* digestive juice (containing 10^5 Fischmann units of β-glucuronidase per ml, and a similar amount of sulphatase) and incubate for 24 hr. at 37°. Extract on a rotatory shaker for 30 min. with 14 ml of $CHCl_3$ or dichloromethane, and twice more with 7 ml of $CHCl_3$ (15 min. each time). Wash the mixed $CHCl_3$ extracts 3 to 5 times with 2·5 ml of 0·1N-NaOH (5 min. each time), then 3 times with 2·5 ml of H_2O (4 min. each time). Evaporate the extracts to dryness, re-dissolve the residues in 5 ml of ethanol and divide the soln. into two parts. In the first, determine the steroids having a propane-1,2-diol chain by the method of Cox. To the second, add 0·2 ml of 5% aq. KBH_4 or $NaBH_4$ soln., set aside for 1 hr., then add 0·2 ml of acetic acid and set aside for 10 min. with occasional shaking. Dry *in vacuo* on a boiling-water bath, re-dissolve the residue in 0·2 ml of acetic acid and determine the reduced steroid by the method of Cox. The difference between the two results corresponds to **I**. The micro-method may be used with one-tenth of the above quantities. Experiments with normal urine showed an average recovery of 93·5%, with a range of 80 to 112%. Results are quoted for normal and pathological urines. R. A. HENDEY

1700. **Assay of catalase for commercial use.** D. Scott and F. E. Hammer (Fermco Laboratories, Inc., 4941 S. Racine Av., Chicago, Ill., U.S.A.). *Enzymologia*, 1960, **22** (3), 194–200 (in English).—A comparison is made between the Keil method (Armour & Co., Bulletin EC-2, 1954), based on the

decomposition of H_2O_2 in an inert atmosphere, and the Baker method (not previously described) in which an aliquot of catalase soln. ($\ngtr$ 1 ml containing $\ngtr$ 3·5 units) is allowed to act upon 100 ml of H_2O_2 soln. (0·5M, buffered with phosphate at pH 7·0) at 25°, until the reaction is complete; 4 ml of this soln. is titrated with 0·25N-$Na_2S_2O_3$ in the presence of H_2SO_4, KI and ammonium molybdate. A blank is performed. One Baker unit is the amount of catalase required to decompose 264 mg of H_2O_2 under the conditions of assay. The effect of N or CO_2 as the inert gas, and of the aliquot size, is studied in the Keil method, which is shown to be satisfactory for liver catalase but not for *Aspergillus* catalase. The effect of aliquot size on the Baker method is considered, and this method is shown to be satisfactory for both liver and fungal catalase. M. A. Ellis

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See also Abstracts—**1340**, Determination of elements in biological systems. **1417**, Determination of cysteine. **1771**, Partition of plant constituents.

Pharmaceutical analysis

1701. **Quantitative isolation of alkaloids from plant materials.** Kum-Tatt Lee (Dept. of Chem., Gov. of the State of Singapore, Outram Road, Singapore). *Nature*, 1960, **188**, 65–66.—Isolate the plant alkaloids as their insol. reineckates, dissolve the ppt. in acetone, and regenerate the alkaloids by passage through a column of De-Acidite FF (OH^- form). Then determine the alkaloids in the eluate by conventional procedures. The method has been applied to the isolation of alkaloids from opium and nux vomica, and to the determination of papaverine and strychnine. A. R. Rogers

1702. **Assay of the sulphates of some alkaloids in non-aqueous medium.** M. Rink, R. Lux and M. Riemhofer (Pharm. Inst., Univ., Bonn, Germany). *Dtsch. ApothZtg*, 1960, **100** (42), 1231–1234.—Dissolve the sample ($\simeq$ 1 milli-equiv.) in warm acetic anhydride (10 ml), cool and titrate with 0·1N-$HClO_4$ in H_2O-free acetic acid. Good results are obtained with the sulphates of quinine, quinidine, sparteine, strychnine, codeine and atropine. Brilliant green and Fettblau B (C.I. Solvent Blue 19) are generally suitable as indicators. A. R. Rogers

1703. **New colour reaction for the detection of micro quantities of strychnine.** N. Stamenova. *Farmatsiya*, 1959, **9** (5), 19–24 (in Bulgarian); *Ref. Zhur., Khim.*, 1960, (17), Abstr. No. 23,733.—In the analysis of mixtures of atropine with strychnine with the Vitali - Morin reaction in an acetone medium, atropine develops a violet coloration which, on the addition of water, is discharged and a golden-yellow colour develops. Pure strychnine treated by the same method gives a similar final coloration, which is specific to strychnine. Brucine gives a similar colour, but only after a blood-red phase which strychnine does not produce. The method is used for the detection of strychnine in the presence of morphine, atropine, hyoscine, quinine, veratrine, ethylmorphine, cocaine and brucine. The reaction is sensitive to 5 μg of strychnine. A. Burwood-Smith

1704. **Modified colorimetric determination of reserpine in pure preparations and tablets.** W. Grabowicz and N. Twierdochlebow (Chemical Works, Pabianice, Poland). *Chem. Anal., Warsaw*, 1960, **5** (3), 401–406.—Reserpine, both as solid and in $CHCl_3$ soln., reacts with bromophenol blue at pH 4 (phosphate - citrate buffer) to form a water-insol. yellow compound which is extracted with $CHCl_3$. The extract is then shaken with 0·1N-NaOH, and the liberated bromophenol blue in the aq. layer, diluted with an equal vol. of 95% ethanol, is measured in a photo-electric colorimeter with a green filter. The error is $\pm$ 1% on 0·015 mg of reserpine in 20 ml. P. Brych

1705. **Scintillation radio-autography of tritium-labelled compounds on paper chromatograms.** E. V. Parups, I. Hoffman and H. R. Jackson (Res. Branch, Canada Dept. of Agric., Ottawa). *Talanta*, 1960, **5** (2), 75–77 (in English).—Tritiated nicotine can be determined by dipping the chromatogram momentarily in a soln. of a scintillating compound (a satd. soln. of anthracene in benzene), allowing it to dry and placing it in contact with fast film (Kodak Royal-X Pan), which is exposed for 1 to 2 weeks. The spot obtained on the film is compared by means of a densitometer with spots obtained from known amounts of tritiated nicotine; 0·38 and 0·19 μC per sq. cm can be detected with exposures of 1 and 2 weeks, respectively. W. T. Carter

1706. **Colorimetric determination of santonin in artemisia.** R. A. Khan and H. Mohiuddin [Glaxo Lab. (Pakistan) Ltd., Karachi]. *J. Pharm. Pharmacol.*, 1960, **12** (9), 544–551.—Santonin reacts with hydroxylamine and $FeCl_3$ to give a purple colour which obeys Beer's law over the range 1 to 5 mg per ml. The results for 5 samples of artemisia agree well with those obtained by the gravimetric method of Massagetov (*Arch. Pharm.*, 1932, **270**, 392) and are about 3% less than those obtained by a volumetric method based on that of Bohme (*Arch. Pharm.*, 1942, **280**, 89). Other lactones, such as artemisin, α-santonin and ψ-santonin give similar colours. *Procedure*—Extract a mixture of the finely powdered flowerheads (2 g) and CaO (0·5 g) with boiling water, extract the santonin with $CHCl_3$ and decolorise the extract by heating with animal charcoal (0·1 g). Evaporate to dryness, dissolve the residue in 18% ethanol, heat again with animal charcoal (0·1 g), filter and adjust the concn. of ethanol to 50% in a total vol. of 50 ml. Mix a 3-ml aliquot with a fresh 7·5% soln. of hydroxylamine in N-NaOH (2 ml), add N-NaOH (5 ml), set aside for 5 min., titrate with N-HCl, to a colourless end-point, with 2:4-dinitrophenol as indicator, and dilute to 50 ml with H_2O; mix a 5-ml aliquot with 2% $FeCl_3$ soln. (1 ml) and measure the extinction within 3 min. at 500 mμ. A. R. Rogers

1707. **Determination of ascaridole in chenopodium oil with hydrogen bromide in acetic acid.** M. I. Blake and R. E. O'Neill (Chem. Div., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1370–1371.—*Procedure*—Shake the oil (150 to 200 mg) with glacial acetic acid (20 ml) and 0·1N-HBr in acetic acid (25 ml) for 5 min., set aside at room temp. for 24 hr. and titrate potentiometrically with 0·1N-Na acetate. Perform a blank determination. The results of 7 assays of one sample of oil ranged from 64·56 to 65·83%; the results of 7 assays of the same sample by the [U.S.] N.F. 1955 method ranged from 64·04 to 66·95%. A. R. Rogers

1708. **The analysis of ternary mixtures by thermomicroscopic methods.** M. Brandstätter-Kuhnert and J. Obkircher (Pharm. Inst., Univ., Innsbruck, Austria). *Mikrochim. Acta,* 1960, (5–6), 836–853 (in German).—The ternary mixtures carbromal - phenacetin - salicylamide and phenazone - phenacetin - phenobarbitone were studied. By plotting the refractive index isotherms of the fused mass and the isotherms of the primary crystals on triangular concn. diagrams, the influence of each factor upon the quant. determination could be found. In each case there was an area unsuitable for measurement where the isotherms were practically parallel; when this was not the case, quant. determination was possible. Precautions should be taken to prevent loss of highly volatile components. P. D. Parr-Richard

1709. **Colorimetric method for the determination of amethocaine alone or in mixtures with atropine or procaine.** N. Stamenova. *Farmatsiya,* 1959, **9** (5), 16–19 (in Bulgarian); *Ref. Zhur., Khim.,* 1960, (17), Abstr. No. 23,732.—The Vitali - Morin colour reaction for atropine is modified specifically for amethocaine (**I**). In the analysis of mixtures of atropine and **I** in an acetone medium, atropine develops a characteristic violet coloration. On the addition of methanol the violet colour is discharged, and a stable ruby-red colour develops. In the analysis of pure **I** by the same method a similar final coloration is observed. It is established that this coloration is specifically due to **I**; pilocarpine, psicaine, cocaine, procaine, cinchocaine and benzocaine do not give a coloration. Beer's law is obeyed, and the reaction is sensitive down to 10 μg of **I**. It is possible to detect **I** in all combinations with procaine and to determine **I** quant. when the ratio of **I** to procaine is $> 1:1$. A. Burwood-Smith

1710. **Quantitative determination of sulphonamides with ion-exchange paper.** E. Lewandowski (Inst. f. allg. Chem., Univ. Poznań, Poland). *Anal. Chim. Acta,* 1960, **23** (4), 317–321 (in German).—Sulphonamides may be separated chromatographically on cation-exchange paper. The zones are rendered visible by spraying with *p*-dimethylaminobenzaldehyde and the area of each zone is directly related to the amount of material present, *e.g.,* for 50 to 200 μg of sulphanilamide, sulphaguanidine and sulphacetamide. T. R. Andrew

1711. **Determination of Paludrine [proguanil].** P. Spacu and I. Albescu (Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.,* 1960, **8** (1), 91–96.—The method is based on the production of a complex with Ni^{2+}. *Procedure*—Between 0·070 and 0·25 g of the sample is dissolved in 30% ethanol and treated with a slight excess of an ammoniacal soln. of $NiCl_2$. The ppt. is collected in a IG4 crucible, washed with cold water and dried at 110°, or dissolved in hot ethanol, and measured spectrophotometrically at 430 mμ. The gravimetric method gives errors of $\simeq \pm 3{\cdot}0\%$. H. Sher

1712. **Determination of methadone and pethidine in some galenical preparations. I. Tablets.** T. Rutschmann (Lab. Pharm. Galénique, Univ., Genève). *Pharm. Acta Helv.,* 1960, **35** (9–10), 482–487 (in French).—*Procedure*—Extract the powdered tablets containing $\simeq$ 150 mg of methadone hydrochloride or $\simeq$ 300 mg of pethidine hydrochloride by shaking for 10 min. at 55° with a mixture of 10% HCl - H_2O (2 : 3) (30 ml) and filter hot. Wash the residue and filter with hot aq. HCl, cool the combined filtrate and washings and dilute to 100 ml. Add aq. NaOH soln. to a 50-ml aliquot until alkaline, extract with several portions of ethyl ether, wash the combined extracts with H_2O and reject the washings. Evaporate the extract to dryness and titrate the residue with HCl. The precision is 3 to 4% in the presence of starch, stearates, alginates and carboxymethylcellulose. Low results may be obtained in the presence of colloidal silicic acid or polyoxyethylene glycol. A. R. Rogers

1713. **Determination of Synopen (halopyramine).** P. Spacu and E. Antonescu (Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.,* 1960, **8** (1), 73–83.—A colorimetric method based on the production of a complex from ammonium reineckate (**I**) and halopyramine (**II**) is proposed. *Procedure*—The acid extract of **II** is treated with a 1% aq. soln. of **I** in the cold. The ppt. is washed with 15 ml of water, then dissolved on the filter with acetone, and the extinction of the deep-red soln. is determined at 533 mμ and compared with standards. The max. error for the range 0·7 to 1 mg of **I** per ml is $-$ 6·0%. Gravimetric, spectrophotometric and potentiometric methods are based on the use of the complex formed with $K_3[Cr(SCN)_6].4H_2O$ (**III**). For gravimetric determinations, the slightly acid soln. of **II** is treated with a conc. soln. of **III** in the cold until the supernatant liquid is violet. After shaking the mixture for 5 min., the ppt. is collected, washed with water till free from Cl^- and dried at 120°. The method has been used for determinations on 0·3 mg with an error of + 1%. For spectrophotometric determinations, the ppt. is dissolved in acetone and the max. extinction is measured with a 574-mμ filter. For the potentiometric method, the ppt. is washed free from Cl^- and dissolved in 20 ml of acetone. The soln. is diluted with water to a slight opalescence and treated with a further 10 ml of acetone. The titration is made with a silver indicator electrode (in a soln. of 0·05N-$AgNO_3$) and a calomel reference electrode. H. Sher

1714. **Gravimetric micro-determination of Flaxedil (gallamine triethiodide).** P. Spacu and E. Antonescu (Chem. Res. Centre, Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.,* 1960, **8** (1), 179–180.—The method is based on the production of an insol. complex from gallamine triethiodide and $K_3[Cr(SCN)_6]$ (**I**). *Procedure*—The sample is acidified with 5 to 6 drops of conc. HCl, then treated with a conc. soln. of **I** until the soln. is violet. The mixture is filtered after 5 min. and the ppt. is oven-dried at 120°. The error is $\pm$ 4%. H. Sher

1715. **Polarographic determination of 4-amino-1,3-dimethyl-5-nitrosouracil.** H. Marciszewski and A. Grzeszkiewicz (Pharm. Inst., Warsaw, Poland). *Chem. Anal., Warsaw,* 1960, **5** (3), 509–510.—The dissolution of samples in water is troublesome and time-consuming; with 0·1N-aq. NH_3 as solvent and Britton and Robinson buffer (pH 6 to 7) as diluent, soln. can be prepared quickly without detriment to stability or subsequent polarography. (*Cf.* Manoušek *et al., Anal. Abstr.,* 1958, **5**, 2249.) P. Brych

See also Abstracts—**1484**, Arsenic in organic matter. **1640**, Determination of piperazine. **1657**, Determination of beeswax in waxes. **1729**, Determination of cyanocobalamin. **1730**, Identification of ascorbic acid. **1731**, Determination of tocopherols.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

1716. **Technique for collection of food volatiles for gas-chromatographic analysis.** W. W. Nawar and I. S. Fagerson (Dept. of Food Technol., Univ. of Mass., Amherst, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1534–1535.—The technique described is a continuous gas - liquid extraction ensuring high recovery of volatiles. The sweep gas, time of sweeping and temperature depend on the sample. The technique has been used for the collection of volatiles from butter oil, maize oil, potato chips, wine, shrimps and apple juice. C. B. Baines

1717. **Estimation of the available lysine in animal-protein foods.** K. J. Carpenter (Sch. of Agric., Univ. of Cambridge, England). *Biochem. J.*, 1960, **77** (3), 604–610.—The reaction with 1-fluoro-2,4-dinitrobenzene for the determination of the free ε-amino-groups of lysine units in purified proteins is applied to animal-protein foods in an attempt to determine the extent of the nutritional damage that may occur through the formation of enzyme-resistant linkages with ε-amino-groups during processing. The dinitrophenyl proteins are hydrolysed with acid without separation from the digest, and the hydrolysates are extracted with ether. The measure of ε-dinitrophenyl-lysine in the aq. layer is based on the further decrease in colour in this layer after treatment with methyl chloroformate and re-extraction with ether. J. N. Ashley

1718. **Gas chromatography in food analysis. I. Determination of the lower fatty acids in foods.** W. Diemair and E. Schams (Univ. Inst. f. Lebensmittelchemie, Frankfurt am Main, Germany). *Z. LebensmittUntersuch.*, 1960, **112** (6), 457–463.—The isolated acids can be satisfactorily separated in the Perkin - Elmer Fractometer (type 116) at 140° with a mixture of sebacic acid and sebacate as the stationary phase in a 2-metre column, and He (100 ml per min.) as carrier gas. A column of a polyoxyethylene glycol is similarly used at 103° for the separation of the aromatic substances of wines. A Hartmann and Braun electronic comparograph is used as detector. *Preparation of samples*: (*i*) *Milk*—Coagulate the sample (150 ml) with 5% H_2SO_4 and remove the fat and curd by centrifugation; make the aq. phase alkaline with $Ca(OH)_2$ soln., extract it with ethyl ether, and then evaporate it nearly to dryness; acidify with HCl and extract the acids with ether; extract the acids into aq. Na_2CO_3 soln., evaporate the aq. phase to dryness, transfer the residue to a small tube, acidify, and extract the acids into ether (0·5 to 1 ml). (A similar alternative procedure involving a steam-distillation under reduced pressure is also described.) (*ii*) *Butter or cheese*—The sodium salts of the acids are obtained in aq. soln., free from fat, by a procedure analogous to that of the Röse - Gottlieb method; the subsequent treatment follows that described for milk. (*iii*) *Wine*—Extract the sample (100 ml) with ethyl ether - pentane (1:1) (3 × 100 ml); separate the acids from the neutral aromatic substances by shaking out with aq. 5% KOH soln.; proceed with the aq. alkaline phase as described for milk. Dry the ether - pentane soln. as thoroughly as possible with anhyd. Na_2SO_4 and concentrate, if necessary, for the chromatographic examination. (*iv*) *Rye bread*—Extract the sample (50 g) with ethyl ether (100 ml); the dried ethereal soln. may be used for direct chromatographic examination or, if necessary, concentrated. Typical chromatograms are given for samples of milk, sherry and rye bread. P. S. Arup

1719. **Absorptiometric determination of fluoride in milk.** Report by Chemical and Metallurgical Services, U.K.A.E.A. (U.K.A.E.A., Risley, Warrington, Ches., England). U.K.A.E.A. Report PG 141(S), 1960. 8 pp.—The method involves curdling, evaporation and ashing of the milk, separation of F^- by steam-distillation, and absorptiometric determination of F^- by its bleaching effect on the aluminium complex of Solochrome Cyanine R (C.I. Mordant Blue 3) (**I**). *Procedure*—to 250 ml of sample warmed to 30° add cheese rennet (1 ml), stir until curdled and set aside for 30 min. Make alkaline to phenolphthalein with 4% NaOH soln. (≮ 5 ml), stir vigorously, set aside for 30 min. and decant the whey into a platinum dish and evaporate. Add the curd, evaporate to dryness and ash at 600°. Leach the ash with 10 ml of H_2O and transfer the contents of the dish to a 250-ml Claissen flask containing 2 g of Ag_2SO_4, rinsing the dish with 50 ml of H_2SO_4 (1:1). Steam-distil at 138° to 140° (liquid temperature), collecting 240 ml with the condenser dipping into 4% NaOH soln. (5 ml), and dilute to 250 ml. Adjust the pH of a 25-ml aliquot to 4·5 with HCl (1:10) or NaOH soln. (4%), add 2 ml of buffer (pH 4·5) (32 g of NH_4Cl, 220 ml of H_2O, 25 ml of glacial acetic acid and 7·5 ml of conc. aq. NH_3), check the pH, and add 15 ml of colour reagent. Dilute to 50 ml, heat in a water bath at 60° for 15 min., cool in cold water for 10 min. and set aside for 30 min. Measure the extinction at 535 mμ in a 1-cm cell against a reagent blank soln. distilled without the sample. Calibrate the spectrophotometer from 0 to 20 μg of F with standard NaF soln. *Colour reagent*—To 13·4 g of NH_4Cl in 450 ml of H_2O add 1 ml of glacial acetic acid, 20 ml of **I** (0·25% in 0·01M-HCl) and 10 ml of $Al_2(SO_4)_3.(NH_4)_2SO_4$ soln. (0·1867%), adjust the pH to 4·5 ± 0·02 with aq. NH_3 and dilute the soln. to 500 ml. Add 1 crystal of thymol, store for ≮ 2 days in amber glass and filter before use. C. S. Howes

1720. **Determination of methoxychlor and/or metabolites in milk following topical application to dairy cows.** M. L. Cluett, W. K. Lowen, H. L. Pease and C. A. Woodhouse (Industrial & Biochemicals Dept., E.I. du Pont de Nemours & Co., Inc., Wilmington, Del.). *J. Agric. Food Chem.*, 1960, **8** (4), 277–281.—Methoxychlor was determined (*i*) by a method based on that of Fairing and Warrington (*Adv. in Chem. Ser.*, No. 1, 1950, 260), involving careful removal of fats, and reaction with H_2SO_4 to give a pink colour measured at 550 mμ, and (*ii*) by determining total organic Cl by solvent extraction of the milk, Pregl catalytic combustion of the extract residue, and spectrophotometric determination of the resulting Cl. Organic Cl-containing compounds other than methoxychlor were not detected. M. D. Anderson

1721. **Rapid determination of mercury in apples by modified Schöniger combustion.** W. H. Gutenmann and D. J. Lisk (Pesticide Residue Lab., Dept. of Entomology, State Coll. of Agric., Cornell Univ., Ithaca, New York). *J. Agric. Food Chem.*, 1960, **8** (4), 306–308.—Loss of Hg by volatilisation during wet-ashing is avoided by using a modified Schöniger combustion. Apple tissue dried on Cellophane overnight *in vacuo* is burned in an

O-filled flask with a rubber-balloon attachment for pressure control. Combustion products are absorbed in 0·1N-HCl, and Hg is extracted by dithizone and determined spectrophotometrically. Recovery of 0·3 to 0·6 p.p.m. of Hg from apples averaged 83·6%. M. D. ANDERSON

1722. **Rapid method for determination of the husk content of barley and oats.** E. T. Whitmore (Plant Breeding Inst., Cambridge, England). *J. Inst. Brewing*, 1960, **66** (5), 407–408.—*Procedure*—The grain (20 g, of known moisture content) is mixed with 100 ml of H_2O containing 20 ml of NaClO soln. (10% of available Cl), NaOH (2·5 g) is added and the mixture is brought gently to the boil and boiled until the husk becomes detached and floats to the surface (approx. 3 min.). The husk is then decanted off, the kernels are thoroughly washed with H_2O, drained, spread on a filter-paper and dried in air overnight. They are then weighed, their moisture content is determined and the husk content obtained by difference. With barley, the results are lower than those by the method of Essery *et al.* (*Ibid.*, 1956, **62**, 150), but correlate well therewith. With oats, the results are higher than those by manual de-husking, and the correlation is not so good as with barley. It is claimed that the present procedure is more accurate than either of the older ones. R. E. E.

1723. **The E.B.C. scale of formazin haze units.** L. R. Bishop (The Brewery, Mortlake, London, S.W.14). *J. Inst. Brewing*, 1960, **66** (5), 388–389.—The Analysis Committee of the European Brewery Convention recommends the following procedure. Prepare a 1% aq. soln. of hydrazine sulphate, setting it aside for at least 4 hr. before use to ensure complete dissolution. Mix an aliquot of this soln. with an equal volume of 10% aq. hexamine soln. and set aside for 24 hr. to complete haze formation. This constitutes "formazin haze concentrate", and is stable for 3 months. Dilute the concentrate with water (1:10) to produce "100-unit E.B.C. haze dispersion", which is stable for 1 week. Suitable dilutions of this can be prepared with water (stable for 1 week) or beer (stable for 6 hr.). Such dilutions can be used for direct or instrumental visual haze comparisons, and for standardising various types of photo-electric instruments. The proportions of light scattered at different angles are similar for beer haze and for formazin haze (Thorne and Nannestad, *Ibid.*, 1959, **65**, 175). R. E. E.

1724. **Rapid method for iodine value and the iodimetric acid value.** W. Ruziczka. *Öst. ChemZtg*, 1960, **61** (10), 298–303 (in German).—The literature relating to the rapid iodine value method of Margoshes and co-workers (*Z. angew. Chem.*, 1924, **37**, 334), as applied to the analysis of unsaturated oils, resins, etc., is reviewed and the iodimetric method of determining acid value due to Kolthoff (*Chem. Weekbl.*, 1926, **23**, 260) is discussed. (37 references.) H. M.

1725. **Gas-liquid chromatography of fatty acid methyl esters: the "carbon number" as a parameter for comparison of columns.** F. P. Woodford and C. M. van Gent (Dept. Phys. Chem., Univ., Leyden, Netherlands). *J. Lipid Res.*, 1960, **1**, 188–190.—The retention times of at least 4 saturated straight-chain fatty acid esters are plotted on semi-logarithmic paper against chain length and a straight line joining the points is drawn. A value corresponding to the retention time of any other chromatographic peak can then be read from the graph, giving the chain length of the hypothetical saturated straight-chain ester which would be eluted at that point; that value is the "carbon number" of the ester on the particular liquid phase employed. Saturated esters have integral "carbon numbers" (*e.g.*, 15·0, 16·0 and 17·0); esters of branched-chain acids and unsaturated acids have not. The "carbon number" is characteristic of a particular ester on a particular liquid phase, and is sufficiently constant over small temp. ranges to allow comparison with other chromatograms, prepared with the same liquid phase in different laboratories. NUTR. ABSTR. REV.

1726. **Gas chromatography of unesterified fatty acids using polyester columns treated with phosphoric acid.** L. D. Metcalfe (Armour Industr. Chem. Co., Chicago, Ill., U.S.A.). *Nature*, 1960, **188**, 142–143.—A mixture (3 µl) of saturated and unsaturated fatty acids (C_{10} to C_{22}) can be separated effectively, in less than 1 hr., on a column (100 cm × 4 mm) of acid-washed Celite (60 to 80 mesh) coated with diethylene glycol adipate polyester (25%, w/w) containing 2% of H_3PO_4. The column temp. is 220° to 235°, the He pressure is 16 lb per sq. in., and a hot-wire detector is used. The peak areas are approx. proportional to the weight percentages of the free acids or their esters. The separation of stearic and oleic acids is incomplete. The methyl esters can be separated on the same column at 180°, only 1 µl of sample being required. W. J. BAKER

1727. **Esterification of fatty acids with diazomethane on a small scale.** H. Schlenk and J. L. Gellerman (Hormel Inst., Univ. of Minnesota, Austin, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1412–1414.—A procedure is described for the preparation of small amounts (0·1 to 0·2 millimole) of diazomethane, which may be labelled with ^{14}C, from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide. The diazomethane is carried by a stream of N into a soln. of the fatty acid in ether which contains 10% of methanol. Esterification is instantaneous and complete. G. BURGER

1728. **Paper chromatography of certain vitamins in phenol and butanol-propionic acid-water solvents.** E. L. Gadsden, C. H. Edwards and G. A. Edwards (Agric. and Tech. Coll. of N. Carolina, Greensboro, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1415–1417.—The literature on chromatography of vitamins is reviewed. The migration of water-soluble and fat-soluble vitamins in two-dimensional chromatography on untreated paper has been studied with buffered water-saturated phenol as the first solvent and butanol-propionic acid-water as the second. The water-soluble vitamins were separated and located by detecting agents. Of the fat-soluble vitamins, only α-tocopherol was located. (42 references.) G. BURGER

1729. **Determination of vitamins and antibiotics by agar diffusion. I. Simplified computations for the plate method.** N. D. Ierusalimskii, I. V. Konova and N. M. Neronova (Inst. Microbiol., Acad Sci., USSR). *Mikrobiologiya*, 1959, **28** (3), 433–443.—The assay of vitamins and antibiotics by the plate method is discussed. It is found that if the recommended three replicate plates are used the mean error of the assay of cyanocobalamin is ± 7·3 ± 3·2% and that of the assay of streptomycin is ± 3·6 ± 2·1%. The use of four parallel plates has no appreciable influence on the accuracy of the

results. A simplified method of computing the amount of the test substance is described, and tables are given that have been constructed for the computation of vitamins and antibiotics.

II. Determinations of cyanocobalamin and its derivatives by paper chromatography. I. V. Konova, N. M. Neronova, N. D. Ierusalimskiĭ and A. I. Borisova. *Ibid.*, 1959, **28** (4), 490–494; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (5), Abstr. No. 5783.—*Procedure*—Chromatograph the vitamin complex in the test liquid, place the paper strips on agar seeded with *Escherichia coli* **113–3**, incubate and then photograph the zones of growth on paper by the contact method. Cut out the impressions of the zones and weigh them. Determine the area by means of the weight. [Knowing the weight of 1 sq. cm of paper, calculate the mean diam. of the zone from the formula $D = 2\sqrt{S/\pi}$, where D is the diam. and S is the area.] Prepare a corresponding nomogram beforehand. Calculate the amount of each component of the vitamin complex from the tables for the cup-plate method. A more reliable method is to add a pure preparation of a component to the soln. before chromatography. It is shown that the cup-plate method and the chromatographic method are equally accurate.
K. R. Cook

1730. **Identification of ascorbic acid.** A. Goudswaard (Rijks-Inst. Pharmacotherap. Onderz., Leiden, Netherlands). *Pharm. Weekbl.*, 1960, **95** (20), 659–660.—The usual procedure for the identification of ascorbic acid (**I**) with $FeSO_4$ is simplified. To a soln. of **I** (0·1 to 1%) are added $CaCO_3$ and $FeSO_4$. After shaking for 1 min. a violet colour is formed. The sensitivity is 1 in 5×10^3 and the colour is fairly stable. Tartaric and oxalic acids interfere and only a yellow colour is formed. Further, it was found that, in the iodoform reaction of Lieben, oxidised **I** is responsible for the pink colour which occurs after addition of iodine and NaOH. The colour intensity reaches its maximum after 30 min., and the colour is then very stable. Maximum absorption is at 510 mμ. The reaction can be used for the identification of **I** in multi-vitamin preparations and in the presence of salicylic acid derivatives.
M. J. Maurice

1731. **Studies on vitamin E. IV. Simultaneous determinations of tocopherols, ubiquinones and ubichromenols (substance SC) in animal tissues: reconsideration of the Keilin - Hartree heart preparation.** A. T. Diplock, J. Green, E. E. Edwin and J. Bunyan (Walton Oaks Exp. Sta., Vitamins Ltd., Tadworth, Surrey, England). *Biochem. J.*, 1960, **76** (3), 563–571.—The method of analysis is based on that of Edwin *et al.* (*Anal. Abstr.*, 1960, **7**, 4506) for tocopherols with several modifications. The tissue (20 g) is homogenised with Na_2SO_4 - acetone at − 70° and extracted for 3 hr. in the dark with acetone. The lipid extract is saponified with saturated aq. KOH - ethanol containing pyrogallol and the hydrolysate is extracted with ethyl ether. An aliquot (10%) of the non-saponifiable extract may be removed at this stage, if required, for the determination of vitamin A by the $SbCl_3$ method. The remainder of the extract is dissolved in methanol and sterols are removed at − 15°. The residue, after evaporation of the methanol, is dissolved in light petroleum (b.p. 40° to 60°), and the soln. is passed through a column of Decalso F (floridin earth is unsuitable). The column is eluted with benzene, and two-dimensional paper chromatography is carried out with 25 or 50% of the eluate as described by Edwin *et al.*, except that 95% (v/v) ethanol is used as the mobile phase for the second dimension. The papers are dried in air, and the spots are observed under u.v. light. Another chromatogram is sprayed heavily with a fresh $FeCl_3$ - 2,2′-dipyridyl reagent to indicate the positions of tocopherol and ubichromenol. The soln. and papers should be shielded as far as possible from daylight. Each clearly separated spot is cut out and eluted. Tocopherols are eluted with 0·07% (w/v) 2,2′-dipyridyl in ethanol, and are determined by the usual method. Ubichromenols, if distinct, are eluted and determined with $FeCl_3$. Combined ubiquinone - ubichromenol spots are eluted with ethanol; one-half of the eluate is used for the determination of ubichromenol, and the other half for the determination of ubiquinone by the borohydride method of Crane *et al.* (*Biochem. Biophys. Acta*, 1959, **32**, 73). Tocopherylquinone and vitamin K_1 are only rarely present, and can be determined by their u.v. spectra.
J. N. Ashley

See also Abstracts—**1482**, Polyphosphates in meat products. **1484**, Arsenic in org. matter. **1577**, Nitrogen in org. materials. **1659**, Destruction of org. matter. **1693**, Cystine in foods. **1756**, Dieldrin in animal fats. **1766**, Hydrometers for milk.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

1732. **Sensitive device for indicating contamination of the air.** B. Kamieński (Inst. of Phys. Chem., Acad. of Sci., Kracow, Poland). *Electrochim. Acta*, 1959, **1**, 278.—The apparatus consists of a very thin (of the order of the mean free path of gas molecules) hydrophilic film containing a colloidal electrolyte, covering the cross-section of a platinum wire (0·01 to 0·9 mm in diam.) melted into a glass rod and joined electrically to a reference electrode. The potential arising from such a device is measured with a valve voltmeter or (better) with a quadrant electrometer, since the internal resistance is of the order of 10^9 to 10^{12} ohms. Very low concn. of a pollutant affect the potential considerably; *e.g.*, a concn. of 0·000007% of Cl in the air causes a shift of 40 mV; the changes are reversible only over a limited concn. range of the contaminant. Organic colloidal electrolytes give films of longer mean life; greater sensitivity is attained with inorganic ones. From a practical standpoint, soap films give good results.
J. Electroanal. Chem. Abstr.

1733. **Spectrographic determination of beryllium in the atmosphere.** M. S. W. Webb (A.E.R.E., Woolwich Outstation, London, England). *Atom*, 1960, (45), 20–31.—Methods for the spectrographic determination of Be in air are reviewed. The usual method is to filter the air and analyse the filter-paper. The effects of the sampling rate, filter medium, and various methods of analysis are discussed. The sampling rate should not be less than the normal breathing rate of man, and the filter medium should capture the clinically important particles of radius 0·4 to 0·8 μ. The effects of filtration velocity on percentage penetration of filter-papers are studied. Glass-fibre papers would seem to be good for this purpose, but unfortunately they yield a beryllium blank, and this must be eliminated for the determination of small amounts of Be. In the analysis of the filter-paper, the best

method is to impregnate it with ferric nitrate soln. and ash it at low temp.; the resulting ferric oxide serves both as a carrier for Be and as a spectrographic buffer. The method is further improved by using photo-electric recording in place of the lengthy photographic process and using a triggered a.c. arc for better Be excitation. Solution methods of analysis of filter-papers are briefly discussed. The disadvantage of these methods is that they require time, and the Churchill - Gillieson monitor, briefly described, was designed for immediate Be monitoring. However, it also has disadvantages: its response varies with particle size, and it has no provision for automatic calibration. A new monitor was therefore designed (called the Woolwich monitor) for analysis within 1 min. after sampling, and it is described in detail. The inefficiency of excitation of condensed sparks was overcome by a modified triggered a.c. arc, the behaviour of which is similar to that of a d.c. plasma arc; its circuit is given together with that for the recording system. Calibration is provided for by means of a spark discharge between a copper and a copper - beryllium electrode, evolving Be at a constant rate. The performance of the monitor was evaluated for beryllium aerosols of narrow particle-size ranges; high concn. of Be, of too short a duration to be detected by filtration techniques, were detected by this monitor. NUCL. SCI. ABSTR.

1734. **Morin method for the detection of beryllium in air samples.** J. Walkley (Mass. Inst. of Technol., Cambridge, U.S.A.). *J. Amer. Ind. Hyg. Ass.*, 1959, (20), **241–245**.—The fluorimetric determination of Be in air with morin, sensitive to **0·004** μg of Be or 0·02 μg per sample, is described. One ml of 0·05M-$Al(NO_3)_3$ and 1 ml of 25% NH_4Cl soln. are added to a 10-ml aliquot of a prepared sample. A drop of phenol red is added, and the soln. is made alkaline with 3N-aq. NH_3 and centrifuged for 10 min. The resulting ppt. is dissolved with 1 ml of 4N-NaOH; 2 drops of 10% KCN soln. are added, and the soln. is diluted to 10 ml. After centrifuging, 1 ml of dil. morin soln. is added, and the fluorescence is measured immediately against a quinine sulphate standard. An aliquot containing 0·01 μg of Be shows no interference at a 100-μg level of Ca, Cu, F, Fe, Mg, PO_4^{3-}, Ti, U or Zr; Zn does not interfere at a level of 75 μg.
CHEM. ABSTR.

1735. **Method for identifying particulate fluoride compounds.** B. J. Tufts (Dept. of Meteorology, Univ. Chicago, U.S.A.). *Anal. Chim. Acta*, **1960**, **23** (3), **209–214** (in English).—The method is intended for the identification of air-borne dust particles collected on a membrane filter. The filter is floated on the reagent soln. [0·057M in Pb, made by mixing 1 part of 10% aq. NaCl soln. with 3·2 parts of 10% aq. $Pb(NO_3)_2$ soln., centrifuging and using the supernatant liquid] until wetted thoroughly. It is then transferred to the surface of water for 2 min., then dried and mounted. With fluorosilicates the pH of the reagent is reduced to 2·5 with acetic acid, and the reagent is soaked on to blotting paper. This gives more compact ppt. In each case the specimen is examined microscopically and the diameters of the crystalline aggregates are measured. The diameter of the ppt. is a measure of the size of the particle which formed it, and calibration graphs are presented for NaF and K_2SiF_6; SO_4^{2-} and PO_4^{3-} give ppt., but these may be recognised by the use of polarised light. Ppt. of F^- and PO_4^{3-} show polarisation colours, whereas those of SO_4^{2-} do not. The PO_4^{3-} colours are less intense, and can be distinguished with practice. H. M.

1736. **Determination of micro amounts of chlorine in air.** E. P. Bŷkov, A. K. Pankova, A. P. Khlŷstov and M. N. Stepochkina. USSR Pat. No. 127,070 (10.3.1960).—The air is drawn at a rate of $\simeq$ 1·5 litres per min. per sq. cm through a paper strip that has been impregnated with a 20% soln. of choline iodide in 90% methanol and dried; Cl is quant. absorbed, forming a yellow spot, the colour of which is compared with standards. The spot may be cut out and treated with 1 ml of water, and the colour of the soln. compared in a microcolorimeter with standard soln. of iodine in 1% choline iodide, containing 0·01 to 1·0 mg of iodine per ml. With low Cl contents, add to the soln. a 0·1% methanolic soln. of *p*-amino-*NN*-dimethylaniline (2 drops per ml of soln.), and compare the resulting red colour with that of soln. containing 0·0005, 0·001, 0·005 or 0·01 mg of iodine per ml, or with permanent standards prepared from soln. of fuchsine in 0·005N-H_2SO_4. The standard soln. of iodine in 1% choline iodide are stable for a month. C. D. KOPKIN

1737. **Method for the determination of tar hydrocarbons in air.** E. Malý (Inst. Hyg. and Ind. Diseases, Bratislava, Czechoslovakia). *Pracovni Lékařstvi*, **1960**, **12** (7), **347–354**.—Liquid paraffin on Whatman No. 4 paper was used as stationary phase and methanol satd. with liquid paraffin as the mobile phase for the ascending chromatographic separation of the 3,4-benzopyrene fraction from other fractions. The semi-quant. determination of 3,4-benzopyrene, separated from pyrene and 1,2-benzopyrene, has been carried out by the planimetric method. The sample of air is drawn through a tube containing three columns of cotton wool moistened with liquid paraffin; the tube is washed out with $CHCl_3$, the $CHCl_3$ is then evaporated to 0·05 to 0·2 ml and placed on the chromatographic paper by means of a Linderström - Lang pipette.
J. ZÝKA

1738. **A new method for the continuous analysis of dissolved oxygen in water.** J. M. Wright and W. T. Lindsay, jun. (Westinghouse Electric Corp., Pittsburgh). *Proc. Amer. Power Conf.*, 1959, **21**, **706–721**.—In the apparatus described, a packed bed of thallium metal is used for the continuous determination of dissolved oxygen in water. Thallium is not attacked by water or dissolved gases other than oxygen. With oxygen it forms thallous oxide which is highly soluble in water, thus increasing the specific conductance of the water. The performance of test and prototype units is described and the results are compared with those of Winkler analyses. More precise measurements are required to confirm the accuracy of the device at concentrations below 0·05 p.p.m. The method appears promising for measurement in the parts per 10^9 range and, perhaps, even lower with suitable modifications. NUCL. SCI. ABSTR.

1739. **Methods for separation and determination of beryllium in sediments and natural waters.** J. R. Merrill, M. Honda and J. R. Arnold (Dept. Chem., Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, **1960**, **32** (11), 1420–1426.—The Be in sea water (5×10^{-13} g per ml) was concentrated by passage through Dowex 50-X8 resin (200 to 400 mesh), the Fe^{3+} or Mn^{2+} form of which had been treated with excess of aq. NH_3, and by elution of Fe with

0·12M-oxalic acid, followed by elution with 6M-HCl (to remove the Be). The Be was then determined spectrophotometrically as the acetylacetone complex (absorption max. at 295 mμ): 0·2 μg of Be can thus be reliably determined. The method is also applicable to ocean-bed and other sedimentary samples, and to the isolation of Be for the measurement of ^{10}Be. J. P. Stern

1740. **Determination of radioactive strontium in water samples.** V. P. Shvedov, T. P. Makarova, L. M. Ivanova and N. A. Pavlova. *Radiokhhimiya*, **1959, 1** (5), 616–618; *Ref. Zhur., Khim.*, 1960, (12), Abstr. No. 45,983.—Treat the dry residue ($\simeq$ 25 g) from evaporation of the sample (50 to 100 litres), together with carriers, with a mixture of 125 ml of HCl (sp. gr. 1·19), 50 ml of HNO_3 (sp. gr. 1·38) and 125 ml of water, with warming. Evaporate the soln. to dryness, dry the residue for 1 hr. at 105° to 110°, dissolve it in 250 ml of 6N-HCl, and evaporate the soln. to dryness; dry the residue as before, and dissolve it by heating for 1 hr. with 200 ml of 0·5N-HCl. Centrifuge off the insoluble residue (containing Si and part of the Sr and Ba) from the soln., which contains the main bulk of Sr, Ba, Ca and other elements, treat it with H_2SO_4 - HF to remove SiO_2, evaporate the acid soln. to dryness, fuse the dry residue with Na_2CO_3, extract the melt with water, and dissolve the $BaCO_3$ and $SrCO_3$ in HCl. Add the soln. to a similar soln. obtained by pptg. the main bulk of the Sr, Ba and Ca as sulphates in the presence of ethanol, converting into carbonates and dissolving in HCl. Precipitate Ba from the combined soln. as $BaCrO_4$, and separate the Sr from Ca by salting out as $Sr(NO_3)_2$ five times with HNO_3 (sp. gr. 1·45 to 1·46). Further purify the Sr by adding Y as carrier, pptg. as oxalate, and igniting to SrO. The activity of the ^{90}Sr is determined by measuring the activity of the daughter ^{90}Y. The hydroxide of Y is purified from Sr by pptg. the Sr as the nitrate, then pptg. Y as the oxalate and igniting to Y_2O_3. The activity of ^{89}Sr and ^{90}Sr is determined by recording the decay curve and analysing it by the rectification method [*Ref. Zhur., Khim.*, 1956, (15), Abstr. No. 45,931]. Methods for the simultaneous determination of the fission products Ag, Sb, etc., present in the samples are briefly described. C. D. Kopkin

1741. **Spectrophotometric determination of fluoride in water.** F. I. Brownley, jun., and C. W. Howle, jun. (Clemson College, Clemson, S.C., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1330–1332.—The method proposed is based on the bleaching effect of F^- on the Th^{IV} - phenylfluorone complex at pH 3·6. Extinctions are measured at 530 mμ. Potential cationic interferences are removed by passage through a column of Amberlite IR-120 (H^+ form). Chloride does not interfere up to 100 p.p.m., but PO_4^{3-} interfere seriously, and if present in concn. > 1 p.p.m. must be separated by distillation. The method is applicable to F^- concn. of 1 to 5 p.p.m. T. R Andrew

1742. **Determination of iodine in mineral waters.** P. V. Rastegina. Publ.: "Thyroid Disease", Kiev, Gosmedizdat, Ukr.SSR, 1959, **2**, 275–278; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,138.—The method is based on extraction of the iodine by precipitation chromatography, its desorption as K_2HgI_4, and colorimetry of the complex HgI_2.CuI. *Procedure*—Make the sample alkaline to phenolphthalein with K_2CO_3, evaporate on a sand bath to 50 ml, filter, wash the residue several times with water, and make the filtrate and washings up to 100 ml. Pass 1 ml of the resulting soln. through a column (8 cm × 0·6 cm) filled with Al_2O_3 (Brockmann) impregnated with $Hg(NO_3)_2$. The resulting mercury halide zones lie in the order HgI_2, $HgBr_2$ and $HgCl_2$. Wash the column with water until the wash-liquor is free from Cl^-; the $HgCl_2$ and $HgBr_2$ are desorbed, while the HgI_2 zone is displaced slightly downwards. Dissolve the ppt. of HgI_2 in anhyd. ether, evaporate the solvent, and dissolve the residue in excess of KI soln. Place drops of the resulting soln. on filter-paper impregnated with a suspension of CuI, and determine the iodine content by comparing the intensity of the orange - red HgI_2.CuI complex with standards. C. D. Kopkin

1743. **[Sludge-digestion] gas analysis by chromatography.** W. L. Henderson. *Wat. & Sewage Wks*, 1960, **107** (8), 312–313.—Digester gas is chromatographed on a silica-gel column with He as carrier gas; O and N are not separated, but this is usually immaterial for this work. A thermal-conductivity detector is employed. The use of the method to follow CO_2 concn. is described. S.C.I. Abstr.

1744. **Colorimetric determination of phenolic materials in refinery waste waters. Removal of sulphides by silver nitrate.** G. E. Gordon (Manufacturing Dept., Standard Oil Co. of California, Richmond, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1325–1326.—The 4-aminophenazone method of the American Petroleum Institute has been modified to eliminate the phenol distillation stage. Sulphides are removed by pptn. with $AgNO_3$ and the excess of Ag is pptd. with NaCl. The results show good agreement with those obtained by the distillation method, are obtained in half the time and are thought to be more accurate. A. R. Rogers

1745. **Determination of β-activity of liquid wastes.** F. Běhounek and V. Zelenková (Fac. Tech. and Nuclear Physics, Prague). *Jaderná Energie*, 1960, **6** (9), 299–302.—The accuracy of the conventional method for the determination of the β-activity of waste waters with an end-window Geiger - Müller tube was increased by the use of double filtration. The determination of the activity of mixtures of radio-isotopes with very different β spectra is thus possible as well as the detection of ^{90}Sr and ^{90}Y. J. Zýka

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See also Abstracts—**1425**, Decaborane in air. **1495**, Hydrogen sulphide in air. **1504**, Control of chromate in waste liquors. **1625**, Aliphatic aldehydes in air. **1639**, Pyrene deriv. in air.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

1746. **X-ray fluorescence determination of zinc in plant tissue.** L. D. Whittig, J. R. Buchanan and A. L. Brown (Univ. of California, Davis, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (5), 419–421.—It has been shown that inconsistent results for Zn are obtained when the intensity of the Zn emission maxima is taken as a function of the Zn concn. in plant tissue of complex and variable composition. For results of high accuracy, known amounts of Zn are added to the dried plant sample, and the amount of Zn in the sample is calculated

on the basis of the increase in emission-to-scatter ratio, or on the increase of actual emission intensity per unit of Zn added. R. A. Hendey

1747. **Rapid method for determining adsorbed sodium and potassium in carbonate soils.** K. Sh. Shatemirov. *Pochvovedenie*, 1960, (2), 107–109; *Ref. Zhur., Khim.*, 1960, (18), Abstr. No. 73,036.—Treat the sample of soil (5 g) with 0·2N-oxalic acid (100 ml × 5), decant the soln., filter and evaporate. Moisten the dry residue in a platinum or nickel dish, evaporate to dryness, heat on a sand bath (to remove excess of oxalic acid) and ignite at 450° to 500° for 2 to 2·5 hr. to convert alkali-metal and alkaline-earth oxalates into carbonates, and iron and aluminium oxalates into oxides. To avoid dissolution of Mg, the alkali-metal carbonates are extracted with satd. aq. MgO soln. (**I**). Filter off the residue, wash it with **I** and dilute the filtrate with **I** to 200 or 500 ml. Titrate an aliquot of the soln. with 0·02N-H_2SO_4 to methyl orange, titrate **I** similarly, and obtain the content of Na and K by difference. The relative error is ± 9% as compared with the gravimetric determination with zinc uranyl acetate and ± 10% as compared with the Gedroits method. C. D. Kopkin

1748. **Simultaneous determination of phosphate and sulphate ions in the presence of metal contaminations [in fertilisers].** L. Szekeres and E. Bakács-Polgár (Inst. of Chem., Univ. of Agric. Sci., Budapest, Hungary). *Magyar Kém. Lapja*, 1960, **15** (10), 460–462; *J. Agric. Food Chem.*, 1960, **8** (5), 417–419.—A volumetric method is described. The sample is dissolved in boiling HCl, and Fe^{3+} and Al^{3+} are masked with EDTA (disodium salt) and Cu^{2+} and Mg^{2+} with 1,2-diaminocyclohexanetetra-acetic acid, both in alkaline soln. The excess of complexan is then destroyed by the addition of $MgCl_2$ soln., with Eriochrome black T as indicator. Ethanol is then added to give a 10% soln. and the phosphate is determined by titration with 0·1M-$MgCl_2$. The ethanol content is then raised to 40% and the sulphate is determined by titration with 0·1M-$BaCl_2$. The results obtained are compared with those given by gravimetric methods. The effects of Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+} and F^- are investigated. B. Vaszko

1749. **Analysis of MCPA/TBA herbicide formulations. I. A liquid - liquid chromatographic method for determination of 2,3,6-trichlorobenzoic acid.** K. Gardner and K. C. Overton (Fisons Pest Control Ltd., Cambridge, England). *Anal. Chim. Acta*, 1960, **23** (3), 271–281 (in English).—With this method, 2,3,6-trichlorobenzoic acid (TBA) can be determined in the presence of all other likely chlorobenzoic acids and chloromethylphenoxyacetic acids. The mobile phase is isopropyl ether, the support is Hyflo Super-Cel, and the stationary phase is a buffer made from 1 vol. of 2M-aq. K_2HPO_4 and 1·5 vol. of 2M-NaH_2PO_4. The sample, containing 2 g of acids, is dissolved in water, acidified with HCl, and extracted several times with ethyl ether. The ether extracts are combined and made up to 200 ml; 1 ml is transferred to the column and washed just into the column with the mobile phase. The mobile phase is then passed at the rate of 2 ml per min. (using pressure of N) and 60 × 5-ml fractions are collected, followed by 2 × 100-ml fractions. Each fraction is titrated with 0·01N-Na methoxide in isopropyl ether, with a specially prepared indicator based on bromothymol blue. The required fractions are Nos. 28 to 60, which will contain one small and one large component. The titre of the latter is a measure of the TBA content. The acids contained in the other fractions are listed.

II. A gas - liquid chromatographic method for the determination of 4-chloro-2-methylphenoxyacetic acid. K. Gardner and K. C. Overton. *Ibid.*, 1960, **23** (4), 337–345 (in English).—After esterification under conditions that prevent esterification of the halogen-substituted benzoic acid impurities, the sample is extracted with dichloromethane, a known quantity of ethyl benzoate is added as an internal standard and the mixture is evaporated in a water bath at 80°. A small aliquot (3 μl) is transferred to a Perkin-Elmer Fractometer having a column of Celite 545 and Apiezon M, and the chromatogram is prepared at a column temp. of 190° with H as carrier gas (50 ml per min.). A chromatogram is reproduced that illustrates the separation of ethyl benzoate, 2-methylphenoxyacetic acid, dichlorobenzoic acids, 6-chloro-2-methylphenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, 2,3,5- and 2,4,5-trichlorobenzoic acids (one peak), 2,3,4-trichlorobenzoic acid and 4,6-dichloro-2-methylphenoxyacetic acid. H. M.

T. R. Andrew

1750. **Determination of α-(4-chloro-2-methylphenoxy)propionic acid in chloromethylphenoxypropionic acids by gas - liquid chromatography with an internal standard.** H. G. Higson and D. Butler (Lankro Chemicals Ltd., Salters Lane, Eccles, Manchester, England). *Analyst*, 1960, **85**, 657–663.—A selective herbicide formulation is based on CMPP, which is a mixture of chloromethylphenoxypropionic acids containing α-(4-chloro-2-methylphenoxy)propionic acid (**I**) as the active ingredient with various proportions of 6-chloro-2-methyl-, 4,6-dichloro-2-methyl- and 2-methylphenoxypropionic acids. To convert the acids into a form suitable for gas - liquid chromatography, they are extracted from acid aq. soln. with $CHCl_3$ and converted into their butyl esters with n-butanol and dry HCl by a specified procedure. The gas - liquid chromatographic apparatus is described. Dimethyl phthalate is used as an internal standard. The method of calculating the content of **I** from the areas under the sample peak and standard peak is described. A modified procedure is given in which an internal standard is not required. A. O. Jones

1751. **Micro-coulometric gas chromatography of pesticides.** D. M. Coulson, L. A. Cavanagh, J. E. de Vries and B. Walther (Dept. of Chem., Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (5), 399–402.—A new rapid screening method is described. The apparatus comprises a chromatography column, a micro-combustion furnace, a power supply for the chromatograph and a coulometer. The chromatographic column used was an aluminium tube (0·25 in. by 6 ft.) packed with 30 to 60-mesh Chromosorb (washed with 6N-HCl, and then H_2O) coated with 15 to 30% (w/w) of Dow - Corning high-vacuum silicone grease (extracted first with ethyl acetate). The coulometer system is essentially that of Coulson and Cavanagh (*Anal. Chem.*, 1960, **32**, 1245) with a more sensitive detector. The chromatograph operates in the conventional manner and effluent gases are mixed with O, burnt in the furnace, and bubbled through the soln. in the titration cell. The resulting Cl or S is coulometrically titrated with an automatic titrator.

For mixed pesticides the time required for each compound to pass through the column must be previously determined, in order to identify the components. The method is rapid ($\simeq$ 1 hr.) and can be used to determine many pesticides (*e.g.*, hexachlorocyclohexane, aldrin, dieldrin, DDT, chlordane, endrin, toxaphene and other chlorinated organic pesticides) in a single operation. Phosphorothioates (*e.g.*, malathion, parathion and Systox) can also be determined. R. A. HENDEY

1752. **Separation and estimation of the four insecticidal constituents of pyrethrum, *Chrysanthemum cinerariaefolium*, by elution chromatography on a column of absorptive charcoal.** H. Stephenson (Pyrethrum Board of Kenya, Nakuru, Kenya). *Pyrethrum Post*, 1960, **5** (4), 22–30.—The four biologically active ingredients of pyrethrum are separated by elution from a charcoal column with light petroleum - ethyl ether (2:3) as solvent. The spectrophotometric evaluation of the fractions is discussed and the following constants are reported—$\lambda_{max.}$ (in light petroleum and in ethanol), cinerin I, 200 mμ and 225 mμ; pyrethrin I, 221 mμ and 224 mμ; cinerin II, 229 mμ and 233 mμ; and pyrethrin II, 227 mμ and 228 mμ; calculated values for ϵ_{227} (in ethanol) were 19,300, 37,400, 25,800 and 46,600, respectively. The method is tedious and not suitable for routine application and is affected by the presence of synergists, surface-active agents and other additives. A sample of commercial pyrethrum extract containing 25% of total "pyrethrins" ("Methods of Analysis," A.O.A.C., 8th Ed., 1955) gave a mean of 23·15% of total "pyrethrins", with a coeff. of variation of 1·81% (13 determinations). The sum of cinerin I and pyrethrin I is close to that obtained by the A.O.A.C. method for "pyrethrins I", but the sum of cinerin II and pyrethrin II is $\simeq$ 85% of the A.O.A.C. "pyrethrins II" result.
H. B. HEATH

1753. **Analysis of crop extracts for traces of chlorinated pesticides by gas - liquid partition chromatography.** E. S. Goodwin, R. Goulden, A. Richardson and J. G. Reynolds (Woodstock Agric. Res. Centre, "Shell" Research Ltd., Sittingbourne, Kent, England). *Chem. & Ind.*, 1960, (39), 1220–1221.—Aldrin and dieldrin in millimicrogram amounts have been detected without prior "clean-up" of the crop or tissue extract. An argon detector is used with a low applied potential, and negative peaks, characteristic of electron capture, are shown for these chlorinated compounds. With a 6-ft. column of 10% (w/w) of E301 silicone on kieselguhr at 230°, and a flow of Ar of 6 litres per hr., the detection limits are 0·05 p.p.m. of aldrin and 0·1 p.p.m. of dieldrin. *pp'*-DDT and γ-BHC show a similar order of detectability, but tend to be degraded on the column, as does endrin, which gives multi-peak chromatograms. R. M. S. HALL

1754. **Cryoscopic determination of the purity of lindane.** R. Handley (Nat. Chem. Lab., Teddington, Middx., England). *J. Appl. Chem.*, 1960, **10** (9), 353–357.—A simple freezing-point apparatus is described. *Procedure*—Powdered lindane (25 g) is melted in the apparatus and dried by the passage of a stream of dry N for 1 hr. During cooling, the temp. is read at 1-min. intervals and the freezing-point is determined. The purity of the sample, in terms of its γ-BHC (**I**) content, is calculated from the observed freezing-point and the freezing-point and cryoscopic depression of pure **I**. Collaborative results from four laboratories show good agreement. The accuracy is $\pm$ 0·1% and results agree with those obtained by the differential refractometric method. A. C. R. HARTLEY

1755. **Residue analysis of a chlorinated insecticide (Thiodan) by combination of gas chromatography and infra-red spectrophotometry.** G. Zweig, T. E. Archer and D. Rubenstein (Pesticide Residue Res., Univ. of California, Davis, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (5), 403–405.—Thiodan (**I**) was used to develop a general method of trace analysis for chlorinated pesticides. The chromatographic column used was a stainless-steel column (0·25 in. by 6 ft.) packed with Dow - Corning No. 11 high-vacuum grease (30% w/w) on 35 to 80-mesh Chromosorb. The column temp. was 225° and the carrier gas was He at a rate of 167 ml per min. Under these conditions the effluent time for **I** was 4 to 7·2 min. The effluent stream was collected in a tapered glass tube containing a pad of glass wool soaked in CS_2, then the tube was washed well with CS_2 (25 ml), and the CS_2 evaporated. The residue (containing 4·8 to 120 μg of **I**) was re-dissolved in CS_2 (0·2 to 5 ml), transferred to a micro-cell (capacity 0·2 ml) for i.r. spectrophotometry, and scanned between 8 and 8·5 μ, with pure CS_2 for the reference beam. The absolute extinction at 8·37 μ was measured and calculated by using the base-line method. Crop material (lucerne, peaches and pears) was extracted (with the roller-stripping technique) and then subjected to the procedure described above. Recoveries of added **I** were 86·4 to 115%, and the absolute sensitivity for **I** was 4 μg per ml. The advantages of the method are simplicity and the simultaneous qual. and quant. analysis of the compounds under investigation. R. A. HENDEY

1756. **Colorimetric determination of dieldrin and its application to animal fat.** C. Cueto, jun. (Communicable Disease Center, Bureau of State Services, Public Health Service, U.S. Dept. of Health, Education and Welfare, Phoenix, Ariz.). *J. Agric. Food Chem.*, 1960, **8** (4), 273–276.—Dieldrin is determined in μg amounts by treatment with diphenylamine in the presence of $ZnCl_2$ to yield a purple colour, which is measured in acetic acid soln. at 650 mμ. The method is applied to dieldrin in animal fat by alkaline hydrolysis of the fat, extraction with hexane, chromatography of the extract on alumina columns to remove impurities, evaporation of the eluate to dryness, and addition of the diphenylamine and $ZnCl_2$ reagents. The alkaline hydrolysis destroys other chlorinated insecticides that might interfere.
M. D. ANDERSON

1757. **Determination of toxaphene by a spectrophotometric diphenylamine procedure.** A. J. Graupner and C. L. Dunn (Res. Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (4), 286–289.—Toxaphene is fused with diphenylamine in the presence of $ZnCl_2$ to give a greenish-blue product which is measured in acetone or acetic acid soln. at 640 mμ. Clean-up procedures for hexane extracts include (*i*) chromatography on a Florisil column, for extracts containing little fat, (*ii*) partitioning between hexane and H_2SO_4 - fuming H_2SO_4, for extracts containing acid-sensitive material, and (*iii*) extraction with dichloromethane - H_2SO_4, for extracts containing much fat, followed by transfer of the toxaphene to hexane, and application of process (*i*). Toxaphene is extracted from formulations with boiling

methanol. Some other chlorinated insecticides may interfere. M. D. ANDERSON

1758. **Colorimetric determination of Guthion residues in crops.** W. R. Meagher, J. M. Adams, C. A. Anderson and D. MacDougall (Chemagro Corp., Kansas City, Mo., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (4), 282–286.—Guthion is separated (*a*) from cotton-seed oil by dissolving the sample in light petroleum, extracting with methyl cyanide and chromatographing on alumina; (*b*) from fruit by macerating the sample with acetone, filtering, adding HCl, and extracting with $CHCl_3$; (*c*) from cole crops by extracting the sample with isopropyl alcohol, and chromatographing on a column of mixed adsorbents; and (*d*) from milk by blending the sample with acetone, filtering, re-extracting the acetone-insol. material with benzene, combining the acetone and benzene extracts, evaporating the solvents, and partitioning the residue between hexane and methyl cyanide; the pesticide passes into the methyl cyanide. Guthion is converted by alkaline hydrolysis into anthranilic acid, which is diazotised, coupled with *N*-1-naphthylethylenediamine dihydrochloride, and measured at 555 mμ. The oxygen analogue of Guthion produces 50 to 70% of the expected colour. The method can also be used for the ethyl homologue of Guthion.
M. D. ANDERSON

1759. **Triphenyltin compounds in crop protection and the determination of residues.** E. Kröller (Bundesgesundheitsamt, Max von Pettenkofer-Inst., Berlin-Dahlem). *Dtsch. LebensmittRdsch.*, 1960, **56** (7), 190–193.—The method involves extraction with dichloromethane, phasic separation of triphenyltin compounds and their water-soluble decomposition products, and determination of Sn after destruction of organic matter and distillation of the Sn as tetrabromide. *Phasic separation*—Cautiously shake an aliquot of the filtered dichloromethane extract (50 ml) with 5% EDTA (disodium salt) soln. (10 ml) and commercial Zephirol soln. (2 ml) and allow to separate. Wash the aq. phase with dichloromethane (10 ml) and shake the combined dichloromethane extracts with 0·5% EDTA (disodium salt) soln. (10 ml). *Distillation of Sn*—To the soln. remaining from the destruction of organic matter with H_2SO_4, HNO_3 and satd. $KMnO_4$ soln. add 50% H_2SO_4 (10 ml) and hydrazine sulphate (1 to 2 g) and distil at 145° to 160° in a current of N by slow addition of a mixture of 6N-HCl (15 ml) and 40% HBr (8 ml) and collect the distillate under water. After removal of Br from the distillate, determine Sn by conventional procedures, *e.g.*, either polarographically or colorimetrically with dithiol. E. C. APLING

1760. **Modifications to a colorimetric method for determining dichlorophen [on textiles].** F. C. Ashton (Min. of Aviation Chem. Inspectorate, H.Q. Building, Royal Arsenal, Woolwich, London). *Analyst*, 1960, **85**, 685–686.—Application of the test described by Gottlieb and Marsh (*Brit. Abstr. C*, 1946, 118), which involves the use of 4-aminophenazone with $K_3Fe(CN)_6$ as oxidising agent, to the determination of dichlorophen (5,5′-dichloro-2,2′-dihydroxydiphenylmethane) (**I**) on textiles showed that $K_3Fe(CN)_6$ is an unsatisfactory oxidising agent for this purpose, but that KIO_4 is satisfactory. Small pieces of the textile sample (1 or 2 g) are extracted with boiling $Na_2B_4O_7$-NaOH buffer soln. (pH 9·7) (4 × 25 ml). The combined extracts are adjusted to 200 ml with the buffer soln. A 2-ml aliquot of the filtered liquid is diluted to ≃ 30 ml with the buffer soln., and 1·5 ml of 1% aq. 4-aminophenazone soln. is added, followed by 10 ml of 0·25% aq. KIO_4 soln. The mixture is diluted to 50 ml with the buffer soln., and the extinction is measured at 510 mμ against a reagent blank and referred to a calibration graph, prepared with a soln. of pure **I** in acetone diluted with the buffer soln. to give a soln. containing 20 μg of **I** per ml. A. O. JONES

1761. **Determination of 2,6-dichloro-4-nitroaniline in ditranil and some fungicidal formulations by infra-red spectroscopy.** P. G. Marshall (Standards Dept., Boots Pure Drug Co. Ltd., Beeston, Nottingham, England). *Analyst*, 1960, **85**, 681–683.—Mixed standards in $CHCl_3$ containing 0·356 to 0·396% of 2,6-dichloro-4-nitroaniline (the active principle of ditranil), 0 to 0·04% of 2-chloro-4-nitroaniline and 0·008% of chloranil (the two impurities present in ditranil) are prepared. The sample (40 mg) is dissolved in 10 ml of $CHCl_3$. The i.r. spectra are recorded over the range 1175 to 1095 cm^{-1} and the base-line absorptions at 1145, 1128 and 1113 cm^{-1} are measured. From the measurements of the standard soln. a calibration graph is plotted from which the amount of each component of the sample is found. With the dust, Allisan, the sample (1 g) is shaken with ether (60 ml) for 30 min., the extract is evaporated, the residue is dissolved in 20 ml of $CHCl_3$ and the i.r. spectrum is recorded at 1145 cm^{-1} as described for ditranil. The spectrum of a standard soln. containing 40 mg of the active ingredients in 20 ml of $CHCl_3$ is recorded similarly. The percentage of active ingredient present is obtained by multiplying the ratio of the base-line absorption of the sample to that of the standard by 4. For a 50% dispersible powder, 0·4 g is shaken with 100 ml of $CHCl_3$ for 30 min. The clear supernatant soln. is used for the i.r. measurement as described for Allisan, with the same standard soln.
A. O. JONES

See also Abstracts—**1750**, Analysis of chloromethylphenoxypropionic acids. **1660**, K in plants. **1662**, Mg in plants. **1667**, V and Co in plants. **1676**, Carotenoids in plants. **1693**, Cystine in feeding-stuffs. **1720**, Methoxychlor in milk. **1774**, F in plants.

5.—GENERAL TECHNIQUE AND APPARATUS

General

1762. **Interchangeable conical ground glass joints.** British Standards Institution (2 Park Street, London, W.1). B.S. 572:1960. 11 pp.—This edition takes into account recommendations under discussion in the International Organisation for Standardisation and aims to ensure that standard joints made in Britain shall be interchangeable with those produced abroad.

1763. **Small rotary sampler and preliminary study of its use.** R. W. M. Hawes and L. D. Muller (Chemical Engng Div., A.E.R.E., Harwell, England). A.E.R.E. Report AERE-R3051, 1960. 22 pp.—The sampler (illustrated) was designed for use with dry ore products. It was intended that the device, which continuously divides the ore into 20 parts, should have a performance superior to that of the microriffle with which it was critically compared, and a statistical analysis of the results suggested

that this was so. The difficulties of designing adequate comparison experiments are considered.
G. J. Hunter

1764. **New hydrogen sulphide apparatus.** C. J. van Nieuwenburg and J. W. L. van Ligten (Techn. Univ., Delft, Netherlands). *Chem. Weekbl.*, **1960**, **56** (40), 550.—A pressure-regulating vessel containing machine oil is described, which is mounted on H_2S cylinders in order to avoid losses of H_2S during the opening and closing of the cylinder.
M. J. Maurice

1765. **Notes on the preparation and construction of silver reductor columns.** J. I. Dinnin (U.S. Geol. Survey, Washington, D.C.). *Anal. Chim. Acta*, 1960, **23** (3), 295–296 (in English).—It is suggested that silver used in reductor columns should be prepared from mixtures of the copper-reduced and electro-deposited types. This allows flow rates to be chosen at will. Pulverised metallic silver and metal platelets may be incorporated with advantage. A suitable column design is described and illustrated that has a siphon type of outflow tube with the outlet above the level of the metal bed. Drying out of the column can thus be avoided.
H. M.

1766. **Density hydrometers for use in milk. Part 1. Apparatus.** British Standards Institution (2 Park Street, London, W.1). B.S. 734: Part 1: 1960. 18 pp.—Specifications are given for three types of hydrometer.

1767. **Improvements in or relating to burettes.** Sartorius-Werke A.-G. Brit. Pat. 854,998; date appl. 31.3.59. Germany, date appl. 24.4.58.—In a burette having a motor-actuated piston, the result of the displacement of the piston in the cylinder is transmitted to an indicating device, *e.g.*, a counting device and/or a digit printing device, the gearing for actuating the piston and the gearing for the indicating device being separated one from the other.
J. M. Jacobs

1768. **An automatic recording titrimeter and its possible uses.** S. Wolf. *Öst. ChemZtg*, 1960, **61** (10), 292–298.—The various electrical methods of indicating the end-point of a titration are discussed, and the use of the Metrohm Potentiograph E-336 as a recorder of titration curves when such techniques are employed is described. With this instrument both normal titration curves and differential curves can be recorded and it may be used with aq. and non-aq. soln. When the instrument is used alone, acid - base and $AgNO_3$ titrations can be followed, and amperometric and constant-current potentiometric titrations are possible. The Potentiograph can be coupled with a Coulometer E-211 for coulometric titrations and with a Konduktoskop E-165 for conductimetric work. Typical titration curves are presented.
H. M.

1769. **Apparatus for use in chemical analysis.** International Analyser Co. Brit. Pat. 848,125; date appl. 31.1.58. Belgium, date appl. 1.2.57.—The apparatus, which enables periodic chemical analyses of an aq. soln. to be made in a completely automatic way, comprises a vessel for containing the aq. soln. to be analysed, a Mariotte vessel to contain the titrating soln. and a collecting vessel to contain a mixture of the soln. and connected to the aq. soln. vessel by a discharge pipe from the latter into which opens an outlet pipe from the titrating soln. vessel. The aq. soln. vessel communicates with the air and is connected to the collecting vessel by a siphon which holds back the soln. in the aq. soln. vessel as long as the level of the aq. soln. is below the level of the top of the siphon. The siphon automatically empties the aq. soln. vessel each time this level is reached, and this constant vol. is delivered at such a rate of flow that a vacuum is created in the discharge pipe, so that in operation a constant vol. of titrating soln. is added, at every discharge, to the aq. soln. flowing through the siphon, the mixture being then collected, for analysing purposes, in the collecting vessel.
J. M. Jacobs

1770. **The 'magnification procedure' in colorimetric ultra-micro titrations with photo-electric determination of the end-point.** J. Mika and B. Szopory (Tech. Univ. f. Heavy Ind., Miskolc, Hungary). *Mikrochim. Acta*, **1960**, (5–6), **729–748** (in German).—The method involves the comparison of the colour of a test soln. treated with reagent in a capillary cell with that of a soln. of relatively large vol., obtained by titrating a known vol. of reagent with a standard soln. of the test material. The method is applied to the determination of Ti with H_2O_2, the error on 2 to 30 μg of TiO_2 being $< \pm 1\%$. Sources of error are discussed in detail.
J. P. Stern

1771. **Methods of liquid - liquid partition.** G. J. Henning (Inst. Verw. Geneeskr. Arom. Gewassen, Groningen, Netherlands). *Pharm. Weekbl.*, **1960**, **95** (20), 645–658.—Multiplicative partition methods (Craig distribution) are discussed and the extraction apparatus of von Metzsch (*Chem.-Ing.-Tech.*, 1950, **22**, 209) is described. Two examples of the application of this technique are given, *viz*, the separation of rutin, hyperin and quercitrin and the analysis of the compounds from hops that are pptd. by lead salts. Discontinuous partition, with repeated addition of the compounds to be analysed, is also discussed and the purification of streptomycin is given as an example. Finally, columns for continuous extraction are described.
M. J. Maurice

1772. **Liquid nitrogen level filler control.** V. E. Schupbach (Goodyear Atomic Corp., Portsmouth, Ohio, U.S.A.). *Anal. Chem.*, **1960**, **32** (11), 1536.—The device, the main component of which is an inverted Hoke HGP valve, is simple and efficient. The operation depends on the temp., and hence the pressure, of a 2-g charge of propane in the sensing element.
C. B. Baines

1773. **The influence of viscometer design on non-Newtonian measurements.** R. McKennell (Ferranti Ltd., Manchester, England). *Anal. Chem.*, **1960**, **32** (11), 1458–1463.—The design described offers uniform shearing conditions and a flexible automatic flow-curve recorder. The effect of shear-rate variation for Newtonian fluids in conventional viscometers is discussed, and various methods for eliminating variations in shear rate, and hence for eliminating the necessity for applying corrections to flow curves for different types of non-Newtonian behaviour, are outlined. The newly designed viscometer is compared with certain industrial viscometers.
C. B. Baines

1774. **Improved multiple all-glass distillation apparatus for determination of fluorine in plant samples.** R. F. Brewer and G. F. Liebig, jun. (Univ. of California Citrus Exp. Station, Riverside, U.S.A.). *Anal. Chem.*, **1960**, **32** (10), **1373**.—With

the apparatus described, and under routine conditions, the quant. transfer of 5 to 2000 μg of F in 350 ml of distillate is achieved in $\simeq$ 50 min. The reproducibility of results is excellent, and the results of duplicate determinations usually agree to within $\pm$ 5%. K. A. PROCTOR

1775. **Improvements in and relating to apparatus for the measurement of the hydrazine content in a solution.** Cambridge Instrument Co., Ltd. [Inventor: H. W. Holy]. Brit. Pat. 848,525; date appl. 20.3.58.—The apparatus comprises a gold (or other noble metal) electrode and a silver - silver chloride electrode immersed in a chloride electrolyte (10% aq. KCl). The arrangement is such that when a soln. under test, *e.g.*, a sample of boiler-feed water, is introduced into the cell, the hydrazine is oxidised on the surface of the gold electrode, thereby causing a current proportional to the hydrazine concn. of the soln. to flow between the gold and the silver - silver chloride electrodes. J. M. JACOBS

1776. **New rapid vacuum fusion apparatus for determining oxygen in titanium and steels.** L. C. Covington and S. J. Bennett (Process Res. Div., Titanium Metals Corp. of America, Henderson, Nev.). *Anal. Chem.*, 1960, **32** (10), 1334–1337.—The apparatus described consists of a resistance-heated furnace, a power supply, a duplicate analytical system and an evacuation system. One operator can complete 75 oxygen determinations in 8 hr. with good precision and accuracy. K. A. PROCTOR

1777. **Simple apparatus for differential thermal analysis.** M. Vaniš and O. Koráb (Inst. Chem. Technol., Prague). *Silikáty*, 1960, **4** (3), 266–270.—Thermo-elements carrying samples are placed in a vertical four-channel tube. Two methods can be used—(*i*) the samples are placed in a furnace which is then heated; (*ii*) the samples are moved into a heated furnace by means of a transferring device. J. ZÝKA

1778. **Simple construction of apparatus for automatic differential thermal analysis.** V. Šatava and Z. Trousil (Inst. Chem. Technol., Prague). *Silikáty*, 1960, **4** (3), 272–277.—A description of an automatic programmed-temp. controller and an apparatus for the direct recording of DTA curves, in which semi-conducting elements are used, is given. J. ZÝKA

1779. **Differential thermal analysis and simultaneous gas analysis.** C. B. Murphy, J. A. Hill and G. P. Schacher (Gen. Engng Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1374–1375.—The equipment described permits the simultaneous collection of gas generated during thermal decomposition and its registration as a peak on the thermogram obtained on differential thermal analysis. K. A. PROCTOR

See also Abstract—**1340**, Progress in equipment and tools for micro-analysis.

Chromatography, ion exchange, electrophoresis

1780. **Relationship between R_F and the composition of the eluent isopropyl alcohol - hydrochloric acid (1:1).** T. Oncescu and S. Zwiebel (C. I. Parhon Univ., Bucharest). *Zhur. Anal. Khim.*, 1960, **15** (4), 409–412.—R_F values were determined for a large number of ions with the eluent isopropyl alcohol - HCl (1:1), with various normalities of HCl, and these were generally in good agreement with those obtained by Carvalho (*Anal. Abstr.*, 1958, **5**, 351), with n-butanol - HCl (1:1) as eluent. Sodium can be satisfactorily separated from K by descending chromatography with 4N-HCl in the eluent mixture (ΔR_F = 0·09); Rb and Cs are well separated with 12N-HCl, group-II elements with 10N-HCl, Zn and Cd with 9N-HCl, Hg from Zn and Cd with low HCl concn., Tl from Al or In with 5·5N-HCl, Be and Al with 10N-HCl, Ca and Cl with 12N-HCl, Zn and Th with 6N-HCl (ΔR_F = 0·11); As^{3+} and As^{5+} with 10N-HCl; U, Th and Zr with 5N-HCl; and Ni and Co with 10N-HCl. There is a parallel relationship between the solubility of the metal chlorides or chloro-complexes and the R_F values. K. R. COOK

1781. **Stable diazo-salts for chromatographic spray reagents.** I. A. Pearl and P. F. McCoy (Inst. Paper Chem., Appleton, Wis., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1407–1410.—The colours developed when 20 phenolic compounds were each sprayed on paper with 30 commercially available stabilised diazo-salts of aromatic amines are reported. The salts used are stable for years. G. BURGER

1782. **New electromechanical integrator, especially for gas-chromatographic analysis.** M. Mohnke and K. Renker (Dtsch. Akad. Wissenschaft., Berlin). *Chem. Tech., Berlin*, 1960, **12** (8), 493–494.—A full description is given of the construction and use of an automatic germanium-diode-actuated photoelectric device for measuring and recording the band areas of the chromatograms, and hence giving automatically the amounts of the components of the gas or vapour. Results are accurate to within 4%. H. L. WHITEHEAD

1783. **Transfer device for gas chromatography.** A. Kreuchunas (DWG Cigar Corp., Detroit, Mich., U.S.A.). *Chemist Analyst*, 1960, **49** (3), 82–83.—The apparatus illustrated allows the transfer of very small fractions to glass capillary tubes for storage, etc. Full constructional details are given. P. D. PARR-RICHARD

1784. **An injection system for gas chromatography.** W. W. Nawar, F. M. Sawyer, E. G. Beltran and I. S. Fagerson (Dept. of Food Technol., Univ. of Mass., Amherts, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1534.—The system described is easily constructed in the laboratory at small cost from readily available materials. A fairly high vacuum can be applied to allow rapid transfer of high-boiling volatiles, with no appreciable sample loss, to almost all types of gas-chromatographic equipment. It is efficient, particularly in application to food volatiles. Recoveries of 90% have been attained with a test mixture containing nine components boiling from 27° to 173·5°. C. B. BAINES

1785. **Apparatus for sampling a fluid and injecting it into a gas-chromatography column.** Distillers Co., Ltd. [Inventor: C. W. Munday]. Brit. Pat. 850,132; date appl. 24.6.58.—The apparatus comprises first and second (perpendicular) lines through which the fluid to be sampled, and the eluting gas passing into the column, respectively, can flow, and a linear tube laterally interrupting these lines. A slidable and non-rotatory plunger, tightly mounted within the tube, is pierced by a passage, the inlet and outlet of which are adapted to connect and be aligned with the interrupted first or second

line, and which is shaped to promote stream-lined flow of fluid through it. Both the plunger and tube are constructed of quartz and their surfaces in contact are ground. J. M. JACOBS

1786. **Gas - liquid chromatography. Programmed-temperature control of the capillary column.** R. Teranishi, C. C. Nimmo and J. Corse (Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1384–1386.—The method described has been developed for the examination of complex natural products boiling over a wide range. Thin-walled stainless-steel capillary tubing is used, giving the advantage of low heat capacity and high heat conductance. Examples described are a complex hydrocarbon mixture and a strawberry flavouring. An argon ionisation detector is used. C. B. BAINES

1787. **Improvements relating to vapour fractometers.** Perkin-Elmer Corp. Brit. Pat. 849,408; date appl. 30.4.59; U.S.A., date appl. 2.6.58.—A preparatory column for a vapour fractometer comprises a number of hollow tubes of equal length packed with an inert material, *e.g.*, diatomaceous earth, supporting a film of liquid substrate developer, *e.g.*, dodecyl phthalate. The tubes are provided at their opposite ends with common end-caps forming a sealing fit with the open ends of the tubes and embodying inlet and outlet connections to the assembly of tubes and connecting conduits between the ends of adjacent tubes. One of the end caps is displaceable in relation to the other to enable the number of tubes connected in series between the inlet and the outlet to be adjusted so as to vary the effective column length, and give the most expeditious and desirable separation of sample mixtures in accordance with their particular physical characteristics as related to vapour fractometry techniques. J. M. JACOBS

1788. **Factors affecting the use of gas - liquid chromatography for the separation of large samples. The column dimensions.** W. J. de Wet and V. Pretorius (Central Tobacco Res. Sta., Kroondal, Transvaal, S. Africa). *Anal. Chem.*, 1960, **32** (11), 1396–1399.—The efficiency of a chromatographic column has been investigated and theoretical and experimental evidence shows that, for a given column efficiency, the max. sample vol. increases as either the column diameter or the column length is increased. C. B. BAINES

1789. **Applications of Carbowax 400 in gas chromatography for extreme aromatic selectivity.** L. R. Durrett (Shell Oil Co., Refinery Lab., Houston, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1393–1396.—This stationary phase is very useful for the selective retention of aromatic hydrocarbons relative to paraffinic hydrocarbons. Two gas-chromatographic methods for the analysis of petroleum samples are modified to use Carbowax 400 as the stationary phase. The determination of aromatic hydrocarbons in aviation petrol is described, and results from 10 aviation blends containing known volumes of benzene and toluene show standard deviations of 0·02% of benzene and 0·05% of toluene, indicating the method to be more accurate than the F.I.A. method for total aromatics. The determination of hydrocarbon impurities in petroleum benzene and toluene is also described, and results show the method to be superior to the ASTM Kattwinkel reagent test. C. B. BAINES

1790. **Molten salt mixtures as liquid phases in gas chromatography.** W. W. Hanneman, C. F. Spencer and J. F. Johnson (California Research Corp., Richmond, U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1386–1388.—This new column permits operation in the temp. range 150° to 400°. Mixtures of the nitrates of Na, K and Li are used as the stationary phase supported on firebrick. Tables are presented showing the resolution of various types of organic compounds. Optimum resolution is attained with samples of 1 μl; this sample size is handled easily with thermal conductivity detectors and has the advantage of linear response. C. B. BAINES

1791. **Use of a carbon monoxide flame detector in gas chromatography.** C. B. Baddiel and C. F. Cullis (Dept. of Chem., Imperial College, London, England). *Chem. & Ind.*, 1960, (37), 1154–1155.—Halogenated methanes were separated on a Johns Manville C22 firebrick column (360 cm $\times$ 4 mm) impregnated with 20% of dinonyl phthalate, and measured with a flame detector. The use of H as the carrier gas led to corrosion by hydrogen halides and to quenching of the flame. These difficulties, together with the variable flow rate due to the high diffusivity of H, were avoided by the use of CO burnt at a wide jet 2 mm in diam. The flow rate of CO was 35 ml per min. and that of air 400 ml per min. In general, the peak area of each compound was linearly related to the sample pressure, but the peak due to chlorotrifluoromethane consisted of two positive parts separated by a negative trough; this is ascribed to combustion variation when different parts of the molecule were burnt. R. M. S. HALL

1792. **A highly sensitive katharometer and its application to the measurement of ethylene and other gases of biological importance.** S. P. Burg and J. A. A. Stolwijk (Harvard Univ., Cambridge, Mass., U.S.A.). *J. Biochem. Microbiol. Technol. Engng*, 1959, **1**, 245–259.—The design and construction of the katharometer are described. It has been found to possess more than 100 times the sensitivity of conventional thermal-conductivity instruments. The equipment is adaptable to the precise determination of ethylene and other gases by gas chromatography. The construction of the instrument and the gas-flow circuit are illustrated. Routine analyses of biologically produced ethylene were conducted and for this purpose the instrument has proved to be about 10^4 times as sensitive as other methods (Young *et al.*, *Amer. J. Botany*, 1959, **35**, 814). Factors influencing the sensitivity of katharometers are considered. CHEM. ABSTR.

1793. **A new type of selective ion exchanger.** J. Seidl and J. Štamberg (Res. Inst. Synth. Resins and Lacquers, Pardubice, Czechoslovakia). *Chem. & Ind.*, 1960, (38), 1190–1191.—A new type of chelate resin has been prepared from fluorone derivatives and formaldehyde. It is selective for Ge even in conc. HCl and is not affected by the presence of As and Fe. N. E.

1794. **Micro-electrophoresis on cellulose acetate membranes.** B. W. Grunbaum, P. L. Kirk and W. A. Atchley (Cancer Res. Inst., Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1960, **32** (10), 1361–1362.—The use of cellulose acetate supporting medium (Kohn, *Clin. Chim. Acta*, 1958, **3**, 450) in conjunction with an apparatus previously described (Grunbaum and Kirk, *Anal. Chem.*, 1960, **32**, 564) is recommended as giving results greatly

superior to those obtained with filter-paper. Staining with Ponceau S (C.I. Acid Red 9) (0·2% in 3% trichloroacetic acid) is preferred as being rapid (10 min.), and easily washed out with 5% acetic acid. H. F. W. KIRKPATRICK

1795. **Ion separation on a thread.** J. Mahon and A. A. Benedetti-Pichler (Brooklyn College, New York, U.S.A.). *Mikrochim. Acta*, 1960, (5–6), 831–835 (in English).—A more sensitive alternative to the ring-oven method for separating metal cations is described. After extraction of the thiocyanates of Fe^{3+}, Co and Zn with ethyl ether, those of Cu and Ni are complexed with pyridine and extracted with $CHCl_3$. Each extract is chromatographed by dipping a piece of acetone-extracted sewing thread into the soln. and the coloured zones are examined by white or u.v. light under the microscope. The colourless $Zn(SCN)_4{}^{2-}$ is identified by its fluorescence reaction with morin. Distinct zones are given by 3 μg of each cation. P. D. PARR-RICHARD

Optical

1796. **Oscillating flat-specimen holder for an X-ray powder camera.** J. D. Wilkinson and L. D. Calvert (Div. of Appl. Chem., N.R.C., Ottawa, Canada). *J. Sci. Instrum.*, 1960, **37** (10), 399–400.—A simple and readily demountable holder for flat specimens, designed to facilitate the direct comparison of films, is described. Details of construction are given. G. SKIRROW

1797. **Causes and control of matrix effects in spectrographic discharges.** A. J. Frisque [Res. and Develop. Dept., Standard Oil Co. (Indiana), Whiting, Ind., U.S.A.]. *Anal. Chem.*, 1960, **32** (11), 1484–1488.—Changes in the discharge temperature resulting from matrix changes have been measured and found to explain the observed intensity-ratio changes. A correction factor based on the discharge temperature provides a significant improvement in analytical accuracy. New requirements for matching line pairs are defined, and the choice of suitable internal standards is discussed. C. B. BAINES

1798. **Elimination of anion interferences in flame spectroscopy. Use of ethylenedinitrilotetra-acetic acid.** A. C. West and W. D. Cooke (Baker Lab., Cornell Univ., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (11), 1471–1474.—In the method described, EDTA is used to minimise or eliminate interference caused by a variety of anions, including phosphate and sulphate, in the determination of Ca, Mg, Co, Cu, Cr and Mn at low concn. The addition of EDTA also enhances the flame emission and greatly stabilises the intensity. The mechanism of this is discussed. Some of the experimental variables in flame spectroscopy are examined, and an instrument is described that has an absolute stability of $\pm$ 2% over a period of 2 months. C. B. BAINES

1799. **Connection between the sensitivity of the determination and the parameters of the spectrographic apparatus.** Z. G. Fratkin. *Zavod. Lab.*, 1960, **26** (8), 971–973.—The effects of various factors, plate contrast, resolution, dispersion, etc., on the sensitivity of spectrographic analysis are discussed. G. S. SMITH

1800. **Modification of Beckman DK-2 spectrophotometer circuitry and operation.** E. Cogan, H. Freund and P. Romas (Albany Metallurgy Res. Center, Bur. of Mines, U.S. Dept. of the Interior, Albany, Oreg.). *Anal. Chim. Acta*, 1960, **23** (3), 294–295 (in English).—By modifying the working procedure the pen travel may be increased so as to give enhanced peak heights. Modification of the circuit, when combined with the above procedure, will give even greater pen travel. The new procedures are described and are stated to give little increase in noise level. H. M.

1801. **Correction of fluorescence spectra and measurement of fluorescence quantum efficiency.** C. A. Parker and W. T. Rees (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Analyst*, 1960, **85**, 587–600.—Commercial spectrofluorimeters record "apparent fluorescence emission and excitation spectra," both of which in some regions of the spectrum are distorted versions of the true spectra, and may be reproducible for the same instrument but differ considerably from results obtained with other instruments of different type. The origin of fluorescence spectra is discussed theoretically. The measurement of true excitation and emission spectra is described. The advantages of using true fluorescence spectra are discussed, and the use of true emission spectra to determine fluorescence quantum efficiencies is described. Standardisation of published spectrofluorimetric data should be achieved when possible. Results for six compounds that fluoresce in the visible region of the spectrum are presented. A. O. JONES

1802. **Effect of organic nitrogen solvents upon specific rotation.** J. Rosin and C. J. Williams (Merck and Co. Inc., Rahway, N.J.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (9), 622–624.—Data are presented to show that aniline, butylamine, 2-aminoethanol, isoquinoline, pyridine and especially quinoline may be used as solvents to enhance the optical rotation of 32 alkaloids, steroids and other drugs, thus increasing the accuracy of identification and assay. The soln. should be protected from strong light during preparation and handling and should be kept for not more than 24 hr. before measurement. A. R. ROGERS

See also Abstract—**1353**, Computer for complementary tristimulus colorimetry. **1451**, Apparatus for determination of Pb.

Electrical

1803. **Alternating-current polarography and tensammetry.** H. H. Bauer (Fac. of Agric., Univ., Sydney, Australia). *J. Electroanal. Chem.*, 1960, **1** (5), 363–378 (in English).—The use of a.c. polarography and tensammetry in chemical analysis and in interpreting reaction mechanisms is discussed, with many examples taken from the literature. Surface-active agents, $WO_4{}^{2-}$ and other non-reducible compounds can be determined by measuring the height of either of the tensammetric waves produced by periodic adsorption/desorption of the species at the electrode/soln. interface. A calibration curve is necessary because peak current *vs.* concn. curves are non-linear. (104 references.) W. J. BAKER

1804. **Rapid polarography.** S. Wolf (Metrohm A.-G., Herisau, Switzerland). *Angew. Chem.*, 1960, **72** (13), 449–454.—By use of a mercury electrode of controlled dropping time of <1 sec., the complete recording time of a polarogram may be reduced by a factor of five. The limiting current is almost completely independent of the potential,

and oscillations are greatly reduced in amplitude. Maxima of the second type are not observed.
A. R. ROGERS

1805. **Vector polarograph.** S. B. Tsfasman. *Zavod. Lab.*, 1960, **26** (7), 888–889.—A sinusoidal voltage of fixed amplitude between 4 and 40 mV is applied simultaneously with the polarising voltage. Since the capacity current is in quadrature with the active component of the electrolytic current a vector-polarogram showing the relation between current and polarising voltage, in which the effect of the capacity current does not appear, can be obtained. Apparatus for this purpose is described. It has a sensitivity of $\simeq 10^{-7}$M and is much simpler in construction than the Barker square-wave polarograph. G. S. SMITH

1806. **New electrode for cathode-ray polarography.** G. E. Penketh (I.C.I. Ltd., Heavy Org. Chem. Div., Billingham, England). *J. Appl. Chem.*, 1960, **10** (8), 324–328.—The polarographic cell consists of two concentric mercury-pool electrodes. The inner electrode forms a rising cathode, in which mercury under a constant head of pressure is allowed to rise and overflow for a fixed time after each potential sweep in order to renew the surface. The sensitivity of the electrode is proportional to surface area, and, with a diameter of 12 mm, $\simeq$0·01 p.p.m. of In^{3+} can be detected and $\simeq$0·05 p.p.m. can be determined. The peak heights are reproducible and are linearly proportional to the concn. of the ion. J. H. WATON

1807. **Simple micro-coulometric arrangement for polarography using the three-electrode system.** J. Mašek (Polarogr. Inst., Czech. Acad. Sci., Prague). *J. Electroanal. Chem.*, 1960, **1** (5), 416–421 (in English).—In the cell described and illustrated, a graphite "lead" from a "Koh-i-Noor" HB pencil forms the working anode, the lower mercury reservoir acts as reference electrode (no current, const. potential), whilst the third electrode is the dropping-mercury type. The vol. of sample soln. is 0·2 ml and the voltage between the dropping electrode and the mercury reservoir is measured with a volt-ohm meter having an input impedance of 50 to 100 MΩ. The cell gave satisfactory results for completely irreversible reactions, *viz*, reduction of H^+ in 0·1M-KCl, of $[Co(NH_3)_6]^{3+}$ in 0·1M-HCl, and of HN_3 in 14M-H_2SO_4. Sources of error are discussed. W. J. BAKER

1808. **Purification of neutral salt solutions for polarographic basal electrolytes from ultra-small amounts of heavy-metal impurities.** E. N. Vinogradova and K. Iobst (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1960, **26** (7), 796–797.—Soln. kept in containers of amber glass tend to lose heavy-metal impurities. Colloidal sulphide of iron in the glass gradually hydrolyses, and the S^{2-} interact with Zn, Pb, Cd and Cu present in the soln. When a soln. of KCl (0·1N) containing Pb (10^{-5}M), Zn (3·5 × 10^{-5}M), Cd (2·5 × 10^{-5}M) and Cu (2 × 10^{-5}M), was passed at a rate of 5 ml per min. through a column (25 cm × 5 cm) of powdered amber glass no trace of the heavy metals could be detected polarographically. G. S. SMITH

1809. **A potentiograph, and automatic registering titration apparatus.** K. Hädicke (Dtsch. Metrohm Fuisting & Co. KG., Essen, Germany). *Fette, Seif., Anstrichmitt.*, 1960, **62** (7), 584–586.—An instrument is described which registers changes in pH, mV or current against the volume of non-aqueous soln. added. It is suitable for titrations involving small potential changes at the end-point in dark media or emulsions. Titration curves are given. The error for pure fatty acids is ±1%, that of a mixture of fatty acids with up to 7 components is ±3%. I. DICKINSON

1810. **Hydrogen electrodes for pH determination and potentiometric titration.** L. N. Davŷdov. *Lab. Delo*, 1960, **6** (4), 54–57.—The micro-electrode described consists of two parts: a pump and a special electrode consisting of two non-communicating chambers (*a* and *b*). Chamber *a* has an internal diameter of 0·4 cm, height 1 cm and a capacity of 0·1256 ml, and is suitable for holding $\simeq$0·06 ml of test liquid. Chamber *b* serves for the saturation by H of the main platinum-black surface. The passage of H into the chamber is controlled by rotating the piston; thus a rotation of 180° cuts off the H supply. The electrode is filled with test soln. by raising the piston. The test soln. is saturated with H by shaking the electrode for 3 to 5 min. Comparative data are given for the pH determination of whole blood, and of phosphate buffer soln. with and without quinhydrone, obtained with different types of hydrogen electrode. A diagram is given of a hydrogen electrode for the determination of pH in potentiometric macro-titration. K. R. COOK

1811. **The relation of catalyst acidity to the electrode potential recorded in an automatic titration.** R. O. Clark, E. V. Ballou and R. T. Barth (Gulf Res. and Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (2), 189–195 (in English).—The surface acidity of catalysts is determined by potentiometric titration of catalyst slurries in methyl cyanide with a standard n-butylamine soln. The method has been successfully adapted for use with an automatic titrimeter and the titration curves produced are in agreement with data obtained from titrations with indicators.
G. S. ROBERTS

1812. **Electrolytic re-oxidation after current reversal in chronopotentiometry.** C. Furlani and G. Morpurgo (Chem. Inst., Univ., Trieste, Italy). *J. Electroanal. Chem.*, 1960, **1** (5), 351–362 (in English).—A mathematical procedure is given for determining the transition time (t') of the re-oxidation that occurs after current reversal at the end of an electrolytic reduction in chronopotentiometry, when the reduced species is unstable and is decomposing according to a first-order reaction. Assuming semi-infinite linear diffusion and equal diffusion coeff. for the reduced and oxidised species, a simple equation relates the ratio of the transition times (t, t') of reduction and re-oxidation with the rate const. (K) of the reaction, independently of all other parameters. The value of K can be determined directly by measurement of $t':t$ experimentally. The validity of the equation has been confirmed for the chronopotentiometric reduction and subsequent re-oxidation of 2 × 10^{-3}M-Fe^{3+} in $\simeq$3M-KOH and 0·1M-triethanolamine, with 0·04 to 0·07M-hydroxyammonium chloride as regenerant for the oxidised species. The method should be useful for the study of electrode processes accompanied by rapid reactions, or for determining labile intermediates during, for example, reduction of metal complexes that undergo previous dissociation.
W. J. BAKER

1813. **Simple device for accurate time-measurement in coulometric analysis.** F. Vorstenburg and A. W. Löffler (Techn. Univ., Delft, Holland). *J. Electroanal. Chem.*, 1960, **1** (5), 422–423 (in English).—The error inherent in the use of a stop-clock during a short electrolysis is minimised by substituting an electronic counter which counts the pulses of a transistorised crystal oscillator having const. frequency *f*. When a diode is included there is no inertia during switch-on and -off, whilst the max. counting error is $1/f$ sec. per measuring period. The circuit is shown. W. J. BAKER

1814. **Automatic measurements and computations for radiochemical analyses.** J. N. Rosholt, jun., and J. R. Dooley, jun. (U.S. Geological Survey, Denver, Colo.). *Anal. Chem.*, 1960, **32** (9), 1093–1098.—Methods of measurement and computation have been developed for the analysis of natural radioactivity which facilitate the large-scale determination of radioactive sources for geochemical studies. K. A. PROCTOR

1815. **Electron affinity spectroscopy—a new method for the identification of functional groups in chemical compounds separated by gas chromatography.** J. E. Lovelock and S. R. Lipsky (Dept. of Internal Med., Yale Univ. Sch. of Med., New Haven, Conn., U.S.A.). *J. Amer. Chem. Soc.* 1960, **82** (2), 431–433.—A simple ionisation chamber is described, containing a small radium source of α-particles. The voltage applied to the chamber may be varied between 0 and 100. The presence of organic vapours in a He gas stream causes an increase or decrease in the intensity of the current flowing through the chamber. It has been found that, for most organic compounds, the electron affinity, which governs the effect in the ionisation chamber, is related to the major functional group. By altering the applied voltage it has been shown that the effects of various types of compound change from positive to negative at particular voltages. By choosing a definite voltage and placing the ionisation chamber in the outlet stream of a gas chromatograph it is possible to distinguish between compounds of different basic structure (*e.g.*, ketones in the presence of hydrocarbons). It is suggested that this device would be of value in qualitative gas chromatography. At present Ar cannot be used as carrier gas, but suggestions are made for modifications which might permit its use. It should then be possible to carry out quantitative measurements with a conventional Ar detector, and to classify the compounds by subsequent passage of the gas stream through the detector described. In its present form the apparatus can be used with N, H or He. T. R. ANDREW

1816. **Interpretation of γ-ray scintillation spectra from fission-product mixtures.** D. H. Peirson (A.E.R.E., Harwell, England). *Brit. J. Appl. Phys.*, 1960, **11** (8), 346–353.—The γ-ray scintillation spectra of fission-product mixtures can be interpreted quant. by reference to standard spectra calculated for the 22 products of the simultaneous slow-neutron fission of ^{235}U. In this way, differences from the standard series can be readily related to differences in fission-product yields or disintegration rates. The decay-scheme and crystal-efficiency data for the standard spectra are tabulated, and the 36 activities (arranged in order of γ-ray energy), together with their corresponding variations in peak-height during 1 to 28 days, are listed. A rapid method of half-life analysis, based on the composite peak-height decay curve, for use when peaks are inadequately resolved by energy is described. Because of an anomaly in spectrometer resolution, the calculated standard peak-height efficiency must be corrected by an empirical relationship determined for the scintillation crystal used in the spectrometer. W. J. BAKER

1817. **Automatic compensation of dead time in pulse-analysis equipment.** D. F. Covell, M. M. Sandomire and M. S. Eichen (U.S. Naval Radiological Defense Lab., San Francisco, Calif.). *Anal. Chem.*, 1960, **32** (9), 1086–1090.—A timing device for the compensation of dead time in an Argonne-type 256-channel analyser has been evaluated and compensation was found to be satisfactory over a range of 500 to 24,000 counts per sec. Because of its simplicity the method is more satisfactory than ultra-fast detectors and circuits. The technique is applicable to problems of dead time in equipment generally. K. A. PROCTOR

1818. **Improved sample-loading technique for solid-source mass spectrometry.** R. E. Powell (Atomic Weapons Res. Estab., Aldermaston, Berks., England). *J. Sci. Instrum.*, 1960, **37** (7), 252–253.—The sample is loaded by evaporation of an aq. soln., dropwise, on a tungsten filament. Heat is provided by holding a soldering iron in contact with the filament supports. By this means the sample is confined to the centre of the filament. G. SKIRROW

See also Abstracts—**1342**, Review of use of nuclear magnetic resonance. **1355**, Chronopotentiometry with current reversal. **1356**, **1357**, Chronopotentiometric potential - time curves. **1370**, Extractive radiometric titration. **1451**, Apparatus for determination of Pb. **1732**, Apparatus for detecting air contamination.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
equivalent	equiv.
ethylenediaminetetra-acetic acid	EDTA
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecule-e, -ar	mol.
normal (concentration)	N
optical rotation	α_l^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$
not greater than	$\ngtr$
is proportional to	$\propto$
less than	$<$
not less than	$\nless$
of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

The chemical nomenclature used in the abstracts is that recommended by The Chemical Society ("Handbook for Chemical Society Authors", The Chemical Society, London, 1960), and may differ from that used in the original articles.

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